

REMARKS

1. Status of claims

Claims 1-3, 5-16, 18-32, and 34-41 are pending.

2. Claim rejections under 35 U.S.C. § 103

The Examiner rejected claims 1-3, 5-16, 18-32, and 34-41 under 35 U.S.C. § 103(a) as being unpatentable over Hoshi et al., US 2005/0222331 or WO 03/091303 ("Hoshi"). (Passages in Hoshi will be cited in the United States publication). Applicants traverse this rejection.

Hoshi teaches compositions comprising (A) a vinyl aromatic hydrocarbon-conjugated diene block copolymer and (B) a vinyl aromatic hydrocarbon polymer which may be (a) styrene, (b) an aliphatic unsaturated carboxylic acid ester-styrene copolymer, or (c) a rubber modified styrene polymer [0070-0073]. No combination of Hoshi component (A) with one or more of Hoshi component (B)(a-c) teaches or suggests the presently claimed composition.

Hoshi component (B)(a) in its most common embodiment would be polystyrene, see [0074]. The resulting polymer in combination with component (A) could be represented as (vinyl aromatic hydrocarbon-conjugated diene block copolymer)-(poly(vinyl aromatic hydrocarbon)). There is no (monovinylarene-alkyl (meth)acrylate copolymer) or (monovinylarene-conjugated diene rubber) present, both of which are recited by the present claims.

Hoshi component (B)(b) in its most common embodiment would be styrene butyl acrylate, see [0076]. The resulting polymer in combination with component (A) could be represented as (vinyl aromatic hydrocarbon-conjugated diene block copolymer)-(vinyl aromatic

hydrocarbon-alkyl (meth)acrylate copolymer). There is no (monovinylarene-conjugated diene rubber) present, as recited by the present claims.

Hoshi component (B)(c) in its most common embodiment would be high impact polystyrene (HIPS), see [0079]. Selection c is “obtained by polymerizing a mixture” of three reactants; 1) vinyl hydrocarbon monomer, 2) a monomer polymerizable with vinyl hydrocarbon monomer, and 3) an elastomeric block, paragraph [0078]. The monomer copolymerizable with vinyl hydrocarbon monomer can be an acrylate or methacrylate. The elastomeric block can be styrene butadiene rubber. Thus, selection c contains an elastomeric block grafted with poly(vinyl aromatic hydrocarbon-alkyl (meth)acrylate). As a result of the grafting the elastomeric block is covalently linked to the grafted poly(vinyl aromatic hydrocarbon-alkyl (meth)acrylate) and the result is a new macromolecule: poly(vinyl aromatic hydrocarbon-alkyl (meth)acrylate)-graft-(elastomeric block). In addition to the new polymer chains grown onto the elastomeric block in the grafting process, the elastomeric block would have undergone two additional significant changes during the grafting process. First, the elastomeric block would have been cross-linked by the free radical polymerization initiators used by Hoshi. Second, in addition to the bulk copolymer of poly(vinyl aromatic hydrocarbon-alkyl (meth)acrylate) surrounding the grafted elastomeric blocks, it is known to the skilled artisan that poly(vinyl aromatic hydrocarbon-alkyl (meth)acrylate) can grow as occlusions within the elastomeric block and can graft to the interior of the elastomeric block. These occlusions increase the volume fraction of the Hoshi selection c macromolecule that is made up by the elastomeric block. In conclusion, the Hoshi selection c macromolecule exhibits significant chemical and microphysical differences relative to the elastomeric block mentioned by Hoshi in paragraph 0078 and as a

result would have significantly different macrophysical properties relative to the elastomeric block *per se*.

The combination of Hoshi compositions (A) and (B)(c) is poly(vinyl hydrocarbon-conjugated diene) blended with poly(vinyl aromatic hydrocarbon-(meth)acrylate) containing domains of poly(vinyl aromatic hydrocarbon-(meth)acrylate)-graft-(elastomeric block) as described above. This is a blend of three polymers different from the blend of three polymers as presently recited (monovinylarene-conjugated diene coupled block copolymer mixed with monovinylarene-alkyl (meth)acrylate copolymer and monovinylarene-conjugated diene rubber). Further, the poly(vinyl aromatic hydrocarbon-(meth)acrylate)-graft-(elastomeric block) is not a rubber and cannot be construed as being a rubber, for the following reasons.

The present claims recite, among other elements, “a monovinylarene-conjugated diene rubber.” The ordinary skilled artisan would understand the plain meaning of this phrase to refer to macromolecules containing monovinylarene units and conjugated diene units wherein the macromolecules have elastomeric (“rubbery”) properties. Among such properties are elastic deformation under stress. This plain meaning is attested by numerous standard references, including *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed. “Styrene-Butadiene Rubber,” vol. 22, pp. 994-995; *Concise Encyclopedia of Polymer Science and Engineering*, “Butadiene Polymers,” pp. 97-100; and *Wikipedia*, “Synthetic Rubber,” http://en.wikipedia.org/w/index.php?title=Synthetic_rubber&printable=yes, accessed by the undersigned April 7, 2006. (Copies of these references are attached for the Examiner’s convenience).

In contrast, Hoshi component B(c) is a styrene polymer grafted to an elastomeric block. Hoshi gives a preferred example of component B(c) as HIPS, high-impact polystyrene [0079].

The properties of Hoshi component B(c) include rigidity, impact resistance, and slipperiness [0079]. The ordinary skilled artisan will understand that a material that has the property of rigidity is not a rubber, regardless of whether it contains elastomeric blocks. This understanding is attested by numerous standard references, including *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed. "Styrene Plastics," vol. 22, pp. 1025-1026; *Concise Encyclopedia of Polymer Science*, *ibid.*, p. 97, which distinguishes styrene-butadiene rubber (SBR) and HIPS; *Concise Encyclopedia of Polymer Science and Engineering*, "Styrene Polymers," p. 1115; *Wikipedia*, "Category:Organic Polymers," http://en.wikipedia.org/w/index.php?title=Category:Organic_polymers&printable=yes, accessed by the undersigned April 7, 2006, which subcategorizes synthetic rubber distinctly from polystyrene; *Wikipedia*, "Polystyrene," <http://en.wikipedia.org/w/index.php?title=Polystyrene&printable=yes>, accessed by the undersigned April 7, 2006. (Copies of these references are attached for the Examiner's convenience). Therefore, the ordinary skilled artisan would conclude Hoshi does not teach a monovinylarene-conjugated diene rubber, as the term is used herein.

If Hoshi component (B) were selected from (b) and (c), the resulting combination of Hoshi compositions (A), (B)(b), and (B)(c), would be poly(vinyl hydrocarbon-conjugated diene) mixed with poly(vinyl hydrocarbon-(meth)acrylate) and poly(vinyl aromatic hydrocarbon-(meth)acrylate)-graft-(elastomeric block). This blend of three macromolecules does not teach or suggest a blend containing monovinylarene-conjugated diene rubber as the term is used herein.

The difference between a monovinylarene-conjugated diene rubber, such as SBR, and HIPS as taught by Hoshi can be seen in their typical uses, *e.g.*, the use of SBR in tires and HIPS in refrigerator liners. SBR is a copolymer of styrene and butadiene. HIPS is styrene

polymerized in the presence of, and in the process grafting onto, an elastomeric block. The Examiner's proposed modification of Hoshi to allegedly arrive at the present claims is so great that it represents a change in the principle of operation of Hoshi (MPEP 2143.01 VI).

For at least these reasons, Applicants request this rejection of claims 1-3, 5-16, 18-32, and 34-41 be withdrawn.

3. *Conclusion*

Applicants submit all pending claims are in condition for allowance. The Examiner is invited to contact the undersigned patent agent at (713) 934-4065 with any questions, comments or suggestions relating to the referenced patent application.

Respectfully submitted,

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ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

FOURTH EDITION

VOLUME **22**

SILICON COMPOUNDS
TO
SUCCINIC ACID AND SUCCINIC ANHYDRIDE



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STYRENE-BUTADIENE RUBBER

Attempts to produce synthetic rubber have been carried out since the 1800s. The introduction of automobiles in the early 1900s gave added impetus to find a substitute for natural rubber, the price of which tripled from \$2.16/kg in 1900 to \$6.73/kg in 1910 (1). The advent of World War I gave Germany incentive to start a crash program on an alternative to natural rubber. From this work, products based on dimethylbutadiene were used, but these were not found to be good substitutes.

In the late 1920s Bayer & Company began reevaluating the emulsion polymerization process of polybutadiene as an improvement over their Buna

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technology, which was based on sodium as a catalyst. Incorporation of styrene (qv) as a comonomer produced a superior polymer compared to polybutadiene. The product Buna S was the precursor of the single largest-volume polymer produced in the 1990s, emulsion styrene-butadiene rubber (ESBR).

When the United States entered World War II, access to the source of natural rubber was eliminated and the federal government set up a consortium of American rubber manufacturers under the auspices of the Office of Rubber Reserve. A total of 15 styrene-butadiene rubber (SBR) plants were constructed between 1941 and 1942. These plants, devoted to the production of a natural rubber substitute, were run by the four principal rubber companies in the United States: Goodyear, U.S. Rubber, B.F. Goodrich, and Firestone. To increase the number of rubber companies participating in the program, two additional companies were formed from smaller rubber producers: Copolymer Corporation and National Synthetic Rubber Corporation (2). The product agreed upon was called GR-S, an abbreviation for Government Rubber-Styrene, and was based on Buna S. It was the standard general-purpose SBR manufactured until right after World War II, when Germany's work on a low temperature system to generate free radicals for cold emulsion polymerization of SBR became known. The properties of this product were so much better than the hot GR-S that the Office of Rubber Reserve ordered all of the consortium's plants to install refrigeration equipment and begin phasing in the cold-polymerized GR-S. This product has been the basis of the emulsion polymer industry in the United States ever since.

In the mid-1950s, the Nobel Prize-winning work of K. Ziegler and G. Natta introduced anionic initiators which allowed the stereospecific polymerization of isoprene to yield high cis-1,4 structure (3,4). At almost the same time, another route to stereospecific polymer architecture by organometallic compounds was announced (5).

In the 1960s, anionic polymerized solution SBR (SSBR) began to challenge emulsion SBR in the automotive tire market. Organolithium compounds allow control of the butadiene microstructure, not possible with ESBR. Because this type of chain polymerization takes place without a termination step, an easy synthesis of block polymers is available, whereby glassy (polystyrene) and rubbery (polybutadiene) segments can be combined in the same molecule. These thermoplastic elastomers (TPE) have found use in nontire applications. Styrene-butadiene-styrene blocks are formed by the anionic solution polymerization technique. The long styrene block portion of the polymer chain imparts a rigidity similar to that of vulcanized rubber. Being thermoplastic, the polymers are easily worked on conventional equipment. Also, because the styrene segments soften on heating, the polymer scrap can be reworked, unlike vulcanized rubber.

Physical Properties

Desirable properties of elastomers include elasticity, abrasion resistance, tensile strength, elongation, modulus, and processibility. These properties are related to and dependent on the average molecular weight and mol wt distribution, polymer macro- and microstructure, branching, gel (cross-linking), and glass-transition temperature (T_g) (see ELASTOMERS, SYNTHETIC).

Emulsion polymerization gives SBR polymer of high molecular weight. Because it is a free-radical-initiated process, the composition of the resultant chains is heterogeneous, with units of styrene and butadiene randomly spaced throughout. Unlike natural rubber, which is polyisoprene of essentially all *cis*-1,4 configuration, giving an ordered structure and hence crystallinity, ESBR is amorphous. For cold ESBR polymerized at 4–10°C, the typical microstructure of the butadiene portion is 72% *trans*-1,4, 12% *cis*-1,4, and 16% 1,2. In hot polymerized ESBR (51.5°C), the typical ratio is changed somewhat to 65% *trans*-1,4, 18.5% *cis*-1,4, and 16.5% 1,2 (6).

Unlike SSBR, the microstructure of which can be modified to change the polymer's T_g , the T_g of ESBR can only be changed by a change in ratio of the monomers. Glass-transition temperature is that temperature where a polymer experiences the onset of segmental motion (7).

For ESBR polymerized at 50°C, knowing the percentage of bound styrene in the copolymer allows estimation of the T_g by the following, where S is the weight fraction of the styrene (% bound styrene) (8).

$$T_g (^{\circ}\text{C}) = (-85 + 135 S)/(1 - 0.5 S) \quad (1)$$

Similarly, for ESBR made at 5°C, the T_g is given by equation 2:

$$T_g (^{\circ}\text{C}) = (-78 + 128 S)/(1 - 0.5 S) \quad (2)$$

The glass-transition temperatures for solution-polymerized SBR as well as ESBR are routinely determined by nuclear magnetic resonance (nmr), differential thermal analysis (dta), or differential scanning calorimetry (dsc).

Among the techniques employed to estimate the average molecular weight distribution of polymers are end-group analysis, dilute solution viscosity, reduction in vapor pressure, ebulliometry, cryoscopy, vapor pressure osmometry, fractionation, hplc, phase distribution chromatography, field flow fractionation, and gel-permeation chromatography (gpc). For routine analysis of SBR polymers, gpc is widely accepted. Table 1 lists a number of physical properties of SBR (random) compared to natural rubber, solution polybutadiene, and SB block copolymer.

Advantages of NR/IR are high resilience and strength, and abrasion-resistance. BR shows low heat buildup in flexing, good resilience, and abrasion-resistance. Random SBR is low in price, wears well, and bonds easily. Block SBR is easily injection-molded, and is not cross-linked. Applications of NR/IR include tires, tubes, belts, bumpers, tubing, gaskets, seals, foamed mattresses, and padding. BR is used in tire treads and mechanical goods, as is random SBR. Block SBR is used in toys, rubber bands, and mechanical goods.

Raw Materials

The monomers, butadiene (qv) and styrene (qv), are the most important ingredients in the manufacture of SBR polymers. For ESBR, the largest single material is water; for solution SBR, the solvent.

Table 1. Properties
Property

density, g/cm ³
tensile strength, MPa ^a
resistivity, Ω·cm, log
dielectric constant at 1 kHz
dissipation factor at 1 kHz
dielectric strength, MV/m ^h
tensile strength MPa ^a
elongation at break, %
hardness, Shore
resilience
stiffening temperature, °C
brittle temperature, °C
continuous high temperature limit, °C

acid
alkali
gasoline and aromatic
hydrocarbon
ketones
chlorinated solvents
oxidation
ozone
γ-radiation

^aRef. 9.

^b*cis*-1,4-Polyisoprene

^c*cis*-1,4-Polybutadiene

^dStyrene-butadiene

^eStyrene-butadiene

^fCross-linked

^gTo convert to

^hTo convert to

Table 1. Properties and Applications of Cross-Linked Rubber Compounds^a

Property	NR/IR ^b	BR ^c	SBR random ^d	SBR block ^e
		<i>Gum stock^f</i>		
density, g/cm ³	0.93	0.93	0.94	0.94–1.03
tensile strength, MPa ^g	17–21	1.4–7	1.4–2.8	11.7–25.5
resistivity, Ω·cm, log	15–17		15	13
dielectric constant at 1 kHz	2.3–3.0	2.3–3.0	3.0	3.4
dissipation factor at 1 kHz	0.0002–0.0003	0.0002–0.0003		
dielectric strength, MV/m ^h				18.9
		<i>Reinforced stock</i>		
tensile strength, MPa ^g	21–28	14–24	14–24	7–21
elongation at break, %	300–700	300–700	300–700	500–1000
hardness, Shore A	20–100	30–100	40–100	40–85
resilience	excellent	excellent	good	excellent
stiffening temperature, °C	–30 to –45	–35 to –50	–20 to –45	–50 to –60
brittle temperature, °C	–60	–70	–60	–70
continuous high temperature limit, °C	100	100	110	65
		<i>Resistance to solvents and conditions</i>		
acid	good	good	good	good
alkali	good	good	good	good
gasoline and oil	poor	poor	poor	poor
aromatic hydrocarbons	poor	poor	poor	poor
ketones	good	good	good	poor
chlorinated solvents	poor	poor	poor	poor
oxidation	good	good	good	good
ozone	poor	poor	poor	poor
γ-radiation	good	good	good	good

^aRef. 9.

^b*cis*-1,4-Polyisoprene, natural rubber (NR), also made synthetically (IR).

^c*cis*-1,4-Polybutadiene.

^dStyrene–butadiene random copolymer, 25 wt % styrene.

^eStyrene–butadiene block copolymer, ~25% SBR styrene (YSBR).

^fCross-linked and unfilled.

^gTo convert MPa to psi, multiply by 145.

^hTo convert MV/m to kV/in., multiply by 25.65.

The quality of the water used in emulsion polymerization has long been known to affect the manufacture of ESBR. Water hardness and other ionic content can directly affect the chemical and mechanical stability of the polymer emulsion (latex). Poor latex stability results in the formation of coagulum in the polymerization stage as well as other parts of the latex handling system.

In converting ESBR latex to the dry rubber form, coagulating chemicals, such as sodium chloride and sulfuric acid, are used to break the latex emulsion. This solution eventually ends up as plant effluent. The polymer crumb must also be washed with water to remove excess acid and salts, which can affect the cure properties and ash content of the polymer. The requirements for large amounts of good-quality fresh water and the handling of the resultant effluent are of utmost importance in the manufacture of ESBR and directly impact on the plant operating costs.

Solution polymerization can use various solvents, primarily aliphatic and aromatic hydrocarbons. The choice of solvent is usually dictated by cost, availability, solvency, toxicity, flammability, and polymer structure. SSBR polymerization depends on recovery and reuse of the solvent for economical operation as well as operation under the air-quality permitting of the local, state, and federal mandates involved.

Styrene. Commercial manufacture of this commodity monomer depends on ethylbenzene, which is converted by several means to a low purity styrene, subsequently distilled to the pure form. A small percentage of styrene is made from the oxidative process, whereby ethylbenzene is oxidized to a hydroperoxide or alcohol and then dehydrated to styrene. A popular commercial route has been the alkylation of benzene to ethylbenzene, with ethylene, after which the crude ethylbenzene is distilled to give high purity ethylbenzene. The ethylbenzene is directly dehydrogenated to styrene monomer in the vapor phase with steam and appropriate catalysts. Most styrene is manufactured by variations of this process. A variety of catalyst systems are used, based on ferric oxide with other components, including potassium salts, which improve the catalytic activity (10).

In 1990, the annual U.S. capacity to manufacture styrene monomer was 4,273,000 t/yr, and production was 3,636,000 t/yr (11). Polystyrene resin is the dominant user of styrene monomer. SBR use is about 7% of U.S. domestic styrene monomer production. Worldwide production in 1995 was projected to be 77% of capacity as demand increased just under 5% per year, from 1990 consumption of 13,771,000 to 17,000,000 metric tons in 1995.

Butadiene. Although butadiene was produced in the United States in the early 1920s, it was not until the start of World War II that significant quantities were produced to meet the war effort. A number of processes were investigated as part of the American Synthetic Rubber Program. Catalytic dehydrogenation of *n*-butenes and *n*-butanes (Houdry process) and thermal cracking of petroleum hydrocarbons were chosen (12).

Economic considerations in the 1990s favor recovering butadiene from by-products in the manufacture of ethylene. Butadiene is a by-product in the C₄ streams from the cracking process. Depending on the feedstocks used in the production of ethylene, the yield of butadiene varies. For use in polymerization, the butadiene must be purified to 99+%. Crude butadiene is separated from C₃ and C₅ components by distillation. Separation of butadiene from other C₄ constituents

is accomplished by commercial methylpyrrolidone worldwide forecasts of 7,166,000; actual total

Soap.

which performs water emulsification of the latex particles.

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Polymerization

ESBR and nitriles: one calls that attention to the units to the ionic initiation

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Emulsion

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is accomplished by salt complexing/solvent extraction. Among the solvents used commercially are acetonitrile, dimethylacetamide, dimethylformamide, and *N*-methylpyrrolidinone (13). Based on the available crude C₄ streams, the world-wide forecasted production is as follows: 1995, 6,712,000; 1996, 6,939,000; 1997, 7,166,000; and 1998, 7,483,000 metric tons (14). As of January 1996, the 1995 actual total was 6,637,000 t.

Soap. A critical ingredient for emulsion polymerization is the soap (qv), which performs a number of key roles, including production of oil (monomer) in water emulsion, provision of the loci for polymerization (micelle), stabilization of the latex particle, and impartation of characteristics to the finished polymer.

Fatty acid soap was first used for ESBR. Its scarcity prompted the investigation of rosin acids from gum and wood as substitutes (1). The discovery of the disproportionation of rosin allowed rosin acid soaps to overcome the polymerization inhibition of untreated rosin acids. Rosin acid soaps gave the added benefit of tack to the finished polymer. In the 1990s, both fatty acid and rosin acid soaps, mainly derived from tall oil, are used in ESBR.

Polymerization

ESBR and SSBR are made from two different addition polymerization techniques: one radical and one ionic. ESBR polymerization is based on free radicals that attack the unsaturation of the monomers, causing addition of monomer units to the end of the polymer chain, whereas the basis for SSBR is by use of ionic initiators (qv).

Free-radical initiation of emulsion copolymers produces a random polymerization in which the trans/cis ratio cannot be controlled. The nature of ESBR free-radical polymerization results in the polymer being heterogeneous, with a broad molecular weight distribution and random copolymer composition. The microstructure is not amenable to manipulation, although the temperature of the polymerization affects the ratio of trans to cis somewhat.

In solution-based polymerization, use of the initiating anionic species allows control over the trans/cis microstructure of the diene portion of the copolymer. In solution SBR, the alkyllithium catalyst allows the 1,2 content to be changed with certain modifying agents such as ethers or amines. The use of anionic initiators to control the molecular weight, molecular weight distribution, and the microstructure of the copolymer has been reviewed (15).

Emulsion Polymerization. Emulsion SBR was commercialized and produced in quantity while the theory of the mechanism was being debated. Harkins was among the earliest researchers to describe the mechanism (16); others were Mark (17) and Flory (18). The theory of emulsion polymerization kinetics by Smith and Ewart is still valid, for the most part, within the framework of monomers of limited solubility (19). There is general agreement in the modern theory of emulsion polymerization that the process proceeds in three distinct phases, as elucidated by Harkins (20): nucleation (initiation), growth (propagation), and completion (termination).

The nucleation stage for sparingly water-soluble monomers, such as styrene and butadiene, lasts up to 15 to 20% conversion of monomer to polymer. Free radicals from some source initiate polymerization in one of four loci: (1) in the

water phase where a free radical attacks a soluble monomer molecule (homolytic nucleation); (2) at some part of the monomer-swollen micelle (micellar nucleation); (3) at the combined surfactant molecule and solvated monomer oligomer in the dispersed phase (nucleation by hydrophobic association); and (4) at the surface of the stabilized monomer droplet. In the first case, the growing oligomer reaches a finite chain length and collapses to form a polymer particle. Available soap then stabilizes this particle. For SBR, the most important source of polymer generation is the micelle. Nucleation by hydrophobic association, similar to homogenous nucleation, forms particles as the oligomer chain reaches a finite length and precipitates out of solution as a particle stabilized with a layer of soap. In the fourth case, because the number of monomer droplets is small in relation to the number of available monomer-swollen micelles, polymer formation in surface area of micelles compared to the monomer droplets and is therefore generally ignored.

The onset of the growth stage is characterized by the disappearance of the micelles. At this point, the growing micelle undergoes a metamorphosis, becoming a polymer particle, now surrounded by a charged layer of surfactant. During this phase, monomer from the shrinking droplets continues to diffuse through the water phase. Polymerization proceeds at a constant rate under steady-state conditions. It is during this stage that free surfactant is made available. The surfactant arises from the following sources: the shrinking monomer droplets, released surfactant from agglomeration of latex particles, and released surfactant from the growing polymer particles which need less surfactant coverage at a larger size because of the surface-to-volume ratio. If enough soap becomes available then more micelles can form. This results in another particle population that gives a bimodal particle distribution. This stage for SBR ends at 55–65% conversion.

The completion stage is identified by the fact that all the monomer has diffused into the growing polymer particles (disappearance of the monomer droplet) and reaction rate drops off precipitously. Because the free radicals that now initiate polymerization in the monomer-swollen latex particle can more readily attack unsaturation of polymer chains, the onset of gel is also characteristic of this third stage. To maintain desirable physical properties of the polymer formed, emulsion SBR is usually terminated just before or at the onset of this stage.

Advantages of emulsion polymerization of SBR include the following: (1) high molecular weight polymer at high rates; (2) relatively low viscosity of the latex formed to give good heat transfer of the generated exotherm; (3) good control of the polymerization temperature; (4) ease of removing unreacted monomers and their recovery; and (5) ease of processing the finished latex into dry polymer product.

The original emulsion SBR was run at high temperature (50°C) using a fatty acid soap system (Table 2). This was because the available free-radical source was potassium peroxydisulfate, $K_2S_2O_8$, which depends on elevated temperature for the production of free radicals (thermal decomposition). It was found early on that dodecyl mercaptan played a key role in the polymerization initiation, as well as in the regulation of the polymer molecular weight. It was proposed

Table 2. Typi

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Table 2. Typical SBR Recipes^a

Table 2. Typical SBR Recipes		Cold SBR	
Elastomer	Hot SBR 1000	1500	1502
Composition, phm			
butadiene	71	71	71
styrene	29	29	29
potassium peroxydisulfate	0.3		
p-menthane hydroperoxide (PMHP)		0.12	0.12
n-dodecyl mercaptan (DDM)	0.5		
t-dodecyl mercaptan (TDM)		0.2	0.18
Emulsifier makeup, phm			
water ^b monomer/water	200	200	200
disproportionated tall oil rosin acid soap	4.5-5	4.5	1.35
hydrogenated tallow fatty acid soap	4.5		3.15
potassium chloride	0.3	0.3	0.3
DARVAN WAQ (secondary emulsifier)		0.1	0.1
Versene Fe-3 (iron complexing agent)		0.01	0.01
sodium dithionate (oxygen scavenger) ^c		0.025	0.025
Sulfoxylate activator makeup, phm			
ferrous sulfate heptahydrate		0.04	0.04
Versene Fe-3		0.06	0.06
sodium formaldehyde sulfoxylate (SFS)		0.06	0.06
Shortstop makeup, phm			
methyl namate	0.05	0.05	0.05
diethylhydroxylamine	0.015	0.015	0.015
Polymerization conditions			
temperature, °C	50	5	5
final conversion, %	72	60-65	60-65
coagulation	acid/amine	acid/amine	acid/amine
antioxidant, ~0.5-0.75 on rubber	stainer	stainer	nonstainer
organic acid content, by weight	5-7	5-7	5-7
styrene content, by weight	24	24	24
mooney viscosity ML-4, min at 100°C	48	46-58	46-58

^aRef. 21.^bMonomer/water ratio adjusted to 1:2.^cpH of solution to 10-10.5.

that the mercaptan radical formed from the action of the persulfate radical as the initiating species for polymerization (22). More recently it has been shown that the enhancement of the mercaptan promoting effect is specific to fatty acid soap containing persulfate-initiated diene systems (23).

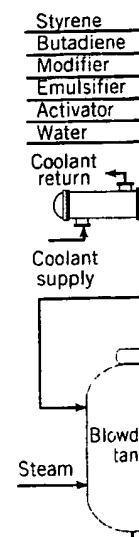
Originally, the production of emulsion SBR was conducted by the batch method, which involves the charging of the entire recipe ingredients at the same time. As the polymerization advances, the amount of solids (polymer) increases. The percentage of solids is related to the percentage of conversion of monomer to polymer. At the proper conversion rate, in this case 75%, a dilute solution of

a chemical called a shortstopping agent is added to the reactor. Hydroquinone, at low levels, is effective. The termination of polymerization is accomplished in two ways. First, shortstopping agents, ie, reducing agents, combine with the initiating species, ie, an oxidizing agent, and effectively destroy the source of free radicals. The second step is to trap and neutralize the free radicals already generated. In the case of hydroquinone, it reduces the persulfate and effectively destroys the generation of any free radicals (24). As it is oxidized to the quinone structure, it becomes an effective free-radical acceptor, scavenging any remaining free radicals.

The shortstopped latex is transferred to one of a series of large vessels, referred to as blowdown tanks, which hold two batches in addition to adequate vapor space. The hot latex is then transferred to large horizontal tanks by pressure differential. These tanks are referred to as flash tanks, for as the latex enters the tank it degasses, that is, releases the residual butadiene, gaseous monomer. The degassed latex is then pumped to the top of a plate column where it is contacted by steam entering the bottom, with the column operating under vacuum. This countercurrent steam distillation of the hot latex efficiently removes the residual styrene monomer. Because SBR contains a high percentage of unsaturation (double bonds) from the butadiene, it is susceptible to degradation by heat, light (uv energy), and O_2 (oxidation). Certain chemicals called antioxidants effectively protect polymers from this degradation. The finished latex containing antioxidant is then subjected to a two-stage coagulation that breaks the emulsion, resulting in a slurry of rubber crumb. The crumb is then passed through a series of washes and dewatering, finally reground and then dried to a low moisture content in large, continuous-belt dryers heated by direct gas-fired burners or steam pipes. The crumb exiting the dryer is then baled in a hydraulic baler in standard 80-lb bales (~36 kg), bagged or film-wrapped, and boxed for shipment in standardized containers.

Through the years, improvements in the finishing process eliminated the need of two-stage coagulation, ie, creaming the latex with sodium chloride and coagulating this agglomerated latex with sulfuric acid. The same results are achieved by mixing the salt and acid and coagulating in one step. To aid the complete coagulation of the SBR latex, small amounts of coagulant aids are added. These coagulant aids are usually based on polyamines. In the mid-1970s, many commercial ESBR manufacturers replaced the brine (NaCl) by increasing the level of polyamine coagulants. A significant benefit from the change was in the reduction of ash residue in the polymer. Single-screw dewatering presses replaced vacuum filters for effective dewatering of the crumb. The screw dewaterers express large amounts of water at its boiling point as a result of the work put into the polymer as it passes through the machine. Soluble salts are released with the water, resulting in lower ash content of the polymer. Figures 1 and 2 illustrate a modern production flow sheet for manufacturing solid ESBR.

Initially, all of the SBR polymer known as GR-S produced during World War II was by the batch process. Later, it was thought that a higher volume of polymer would be needed for the war effort. The answer was found in switching from batchwise to continuous production. This was demonstrated in 1944 at the Houston, Texas synthetic rubber plant operated by The Goodyear Tire & Rubber Company. One line, consisting of 12 reactors, was lined up in a continuous



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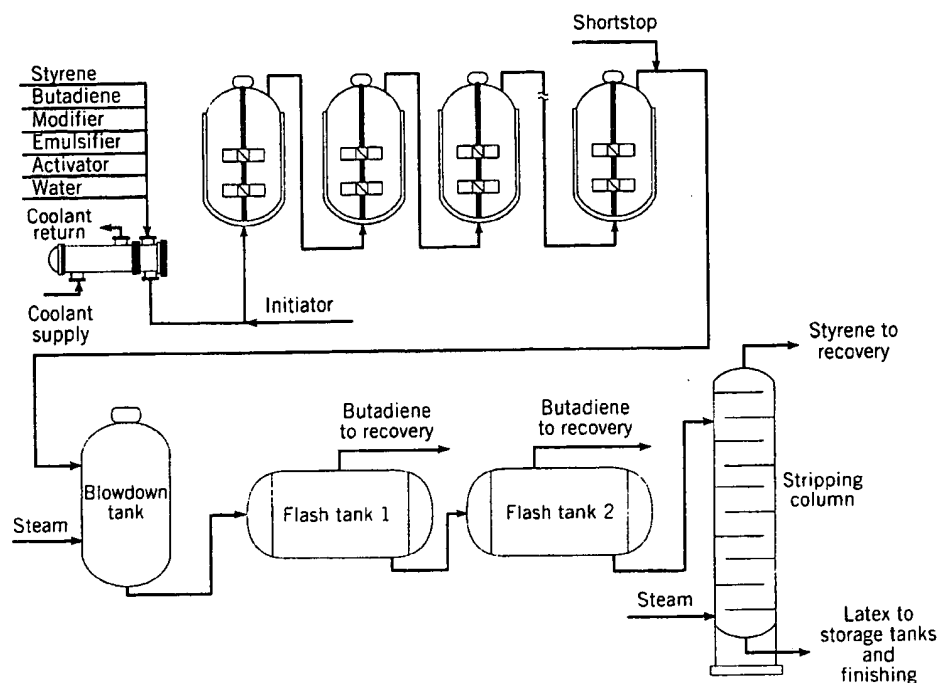


Fig. 1. Typical continuous emulsion SBR polymerization.

mode, producing GR-S that was more consistent than the batch-produced polymer (25). In addition to increased productivity, improved operation of the recovery of monomers resulted because of increased (20%) reactor capacity as well as consistent operation instead of up and down, as by batchwise polymerization.

Continuous polymerization is accomplished by making up all recipe ingredients in solutions, which are mixed with the monomer streams, brought to desired temperature, and initiated by addition of the free-radical source. Of critical importance is the accurate makeup of the solutions and precise metering of all the streams. Modern ESBR plants depend on computer control (distributive control systems). The reactors are connected in series so that the liquid flow is into the bottom and out the top of each agitated vessel. The residence time in the reactor train is controlled by either a variable volume last reactor or a series of large-diameter pipes (displacement columns), whereby at the correct solids percentage (conversion), the shortstop is added to the exiting latex (see Fig. 1).

After World War II, it was reported that the Germans had been working on a cold emulsion polymerization based on a redox initiation system that gave far superior SBR to the conventional hot polymerization (see Table 2). The principal differences were a polymerization temperature of 5°C instead of 50°C, monomer-to-polymer conversion of 60–65% instead of 75%, and the use of a reduction/oxidation system (redox) to supply free radicals by chemical rather than thermal means. The superiority of cold over hot SBR was attributed, in part, to the greater linearity and less gel of the cold polymer. It was shown that in the cross-linking reaction of butadiene, the ratio of the rate of cross-

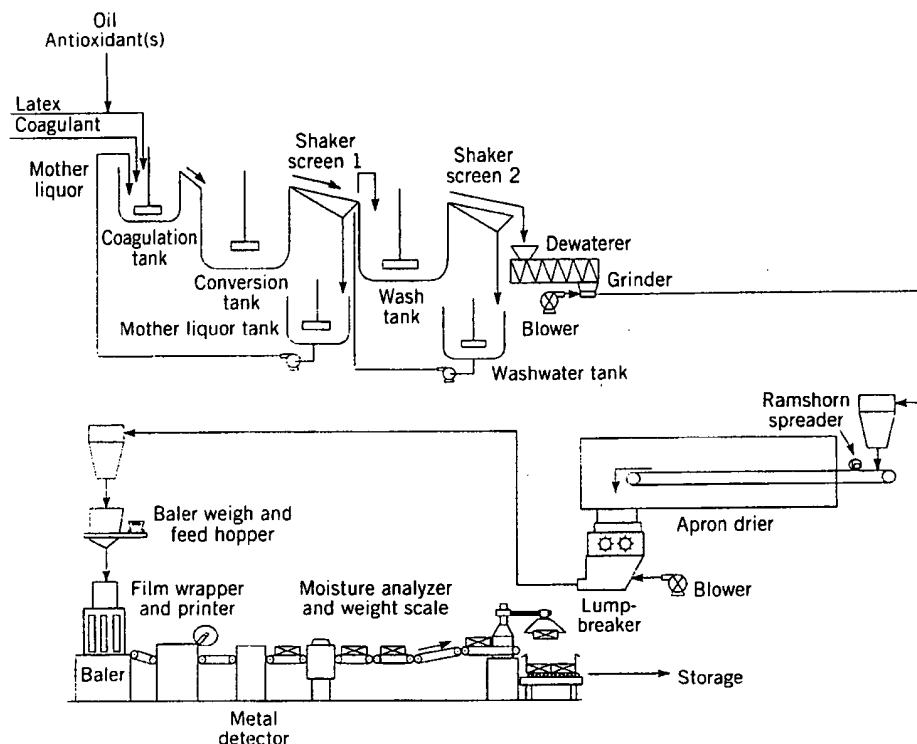


Fig. 2. Typical emulsion SBR finishing.

linking to the rate of propagation is constant up to the point where the monomer phase disappears (26). This ratio decreases as the polymerization temperature is lowered. Thus, there are fewer cross-linking sites at lower temperatures. At the point of monomer depletion (Smith-Ewart third stage), cross-linking increases rapidly. By lowering the conversion rate at which the polymerization is terminated, that point is not reached.

The impact of cold GR-S was quite pronounced. The U.S. government edicted that all of the emulsion SBR plants switch to the cold process. This required addition of refrigeration capacity in these plants as well as other significant changes, such as insulation of reactors, improved vacuum to reduce oxygen that retards polymerization, and the heating of latex in blowdown tanks to aid in the disengagement of butadiene when transferred to the flash tanks.

It was found that cold emulsion SBR could be made at very high molecular weight, combined with petroleum-based oils at a very high level. Although the polymer could take up oil to the extent of 60 parts of oil per 100 parts of polymer, a standard level of 37.5 parts of oil per 100 parts of polymer was established because the plasticizing power of the oil would require extremely high polymer molecular weight at the 60 part level. The oil was added to the latex as an emulsion and cocoagulated in the standard system. The resultant oil-extended polymer had the benefits of very high molecular weight (improved stress-strain properties) with the processibility of medium Mooney viscosity SBR. Extending

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pure polymer with oil increased the amount of product over 25%. In addition, the economics of oil-extended SBR was quite attractive considering that a 36-kg bale contained about 10 kg of a low cost process oil.

Several different petroleum process oils are used as extenders for SBR. These are classified as highly aromatic, aromatic, naphthenic, and paraffinic. The highly aromatic oils give the most desirable physical properties to the polymer and are widely used in tire treadstock. However, these oils impart a black color to the polymer and produce staining, ie, discoloration of light-colored articles that come in contact with products containing the oil. For light-colored articles and products in contact with light-colored materials, naphthenic or paraffinic oils are preferred.

The properties of emulsion SBR are comparable to those of natural rubber only when SBR is reinforced with carbon black. Carbon black can be slurried in water and then combined with the SBR latex and cocoagulated to give a product called black masterbatch. The black masterbatch would require considerably less time and energy to get the carbon black dispersed in the nonproductive compound than if it were dry-mixed with the polymer. Other advantages of handling black masterbatch are the elimination of inventorying and handling carbon black, less energy demand in mixing stocks, and better dispersability of the carbon black in the compound.

Black masterbatch can be made with or without oil-extended SBR. Commercially there are available, worldwide, 11 numbered ESBK cold black masterbatches and 15 ESBK cold oil-black masterbatches (27). These types range in black type and content as well as oil type and amount. Of course, not every listed product is available from every supplier.

Solution SBR. Addition polymerization is accomplished in three steps: initiation, propagation, and termination. The alkylolithium-initiated polymerization in hydrocarbon solvent has no termination step, resulting in living polymer. The mechanism for initiation is thought to be dependant on the addition of the lithium alkyl across the vinyl double bond giving an organolithium compound. Propagation is effected by the further addition of monomer as a stepwise reaction, reforming the same type of carbon-lithium bond (28).

Without the termination step in the alkylolithium polymerization, the batch polymerization results in a copolymer composition of styrene and butadiene that markedly changes with polymer conversion. This produces blockiness, ie, long segments of one constituent in the copolymer chains. An explanation for this behavior is that the butadiene reactivity is considerably greater than that of styrene in the copolymerization and has been shown to be caused by the high cross-propagation rate of the styryllithium anion (29). This mechanism actually allows great flexibility in producing very different types of polymers. The so-called tapered block polymer is made by polymerizing styrene and butadiene monomers with butyllithium as the initiator. By addition of certain chemicals such as ethers, tertiary amines, and phosphites, random distribution of the comonomers is achieved. Certain of these additives also affect the microstructure of the butadiene portion. It is thus possible to control polymer composition, monomer distribution sequence, microstructure (trans-1,4/cis-1,4 ratio constant at variable vinyl level), molecular weight, molecular weight distribution, and polymer chain structure. Figure 3 shows a flow diagram for the continuous production of solution SBR. The kinetics of alkylolithium solution copolymerization

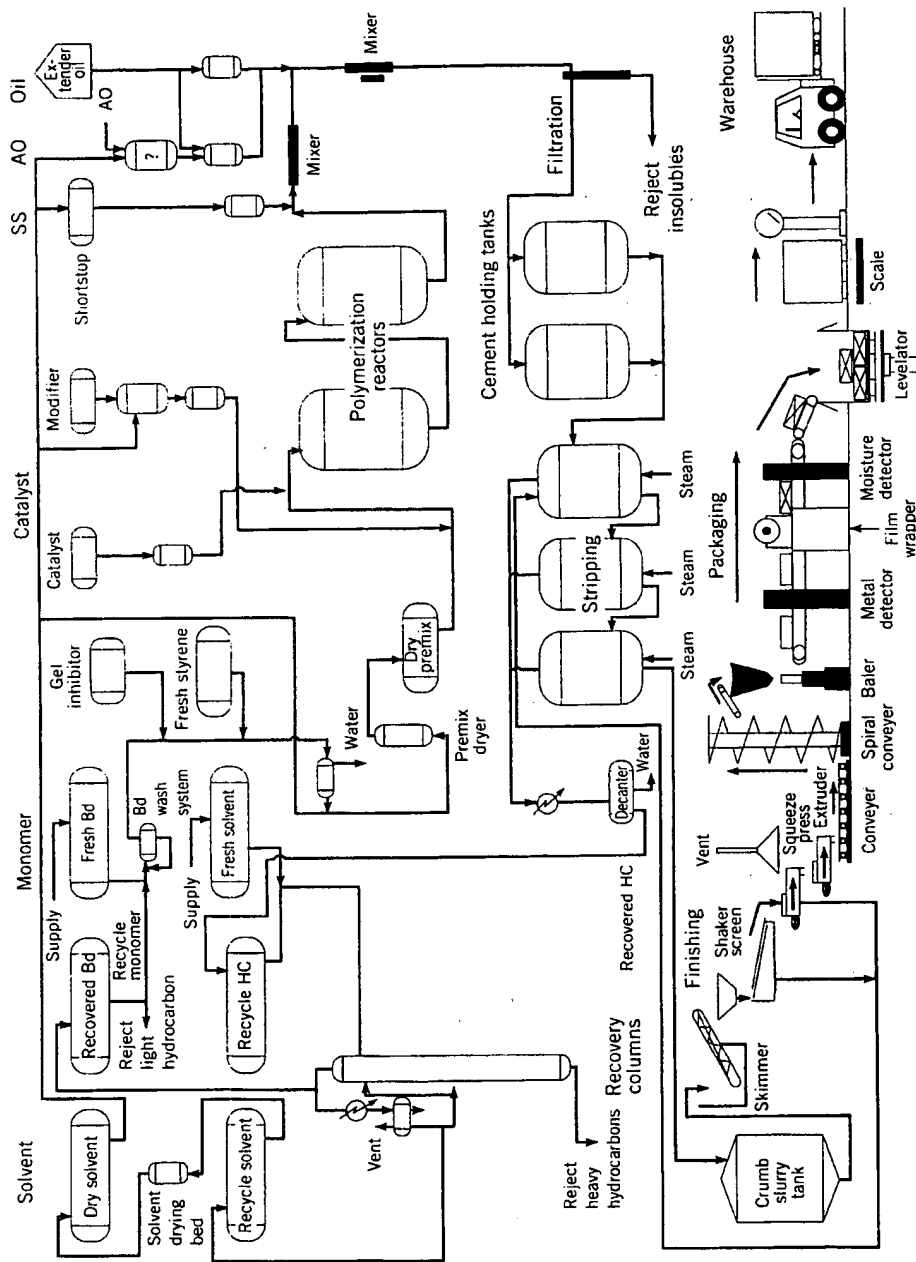


Fig. 3. Solution SBR manufacture by continuous process where Bd = butadiene, HC = hydrocarbon, AO = antioxidant, and SS = shortstop.

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of styrene and butadiene in hydrocarbon solvent, along with techniques to randomize the resultant polymer, have been reviewed (30).

Once the ability to control the randomization of solution SBR was understood and established, the commercialized SSBR began to displace some of the ESBR in tire applications. It was found that the SSBR alone could achieve the same desired properties that blends of ESBR and polybutadiene gave, thus simplifying the compound recipes. The combination of low rolling resistance and high wet traction without sacrificing abrasion resistance (tread wear) is attainable with SSBR but not with ESBR alone. Also, by controlling the vinyl microstructure to a low level, a lower T_g is achieved than for ESBR at the same styrene content. This allows for a higher level of oil and carbon black to be added (31).

Because the styrene segments of block copolymers soften on heating, properties that depend on stiffness, hardness, abrasion, etc., may suffer. Conversely, the polymers flow much more readily on molding, extruding, etc. This property allows them to be used in shoe soles and wire insulation applications. Until more recently, the use of block SSBR in tire tread applications was not considered because of the significantly higher running temperature associated with compounds containing them. A Japanese patent claims that the use of a low molecular weight random block copolymer of styrene and butadiene (A-B-A block SSBR) as part of a tire tread composition imparts improved grip (adhesion) and abrasion resistance to the tire (32).

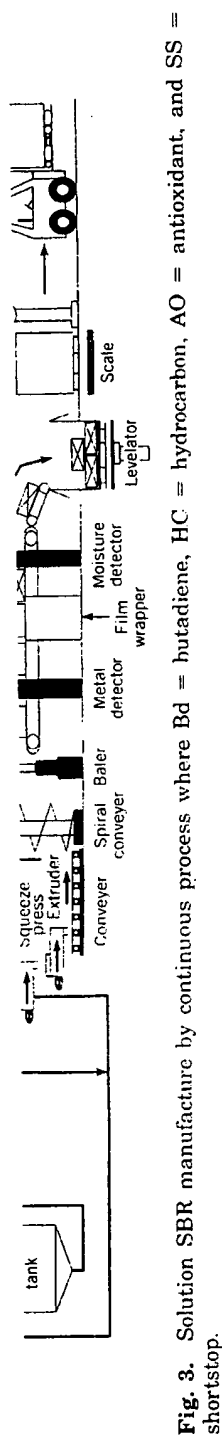
SBR Compounding and Processing

The initial production of GR-S rubber required a learning period in processing before rubber workers were comfortable with the new synthetic rubber. Although softer and more plastic initially, the GR-S did not break down as much as natural rubber. Once familiar with the differences, processing GR-S was handled quite comfortably. The same was true when the cold GR-S was introduced, followed by the oil-extended version, and SSBR.

Development of the Mooney viscometer gave compounders an indication of the processibility of different lots of the uncompounded polymer. This machine measures the torque resistance encountered by a rotor revolving in a chamber surrounded by polymer at a constant temperature. The resulting Mooney number describes the toughness of the polymer and is an indirect measure of molecular weight.

Gel, the insoluble fraction of polymer formed by high conversion of monomer to polymer, excessive mixing, poor antioxidant protection, etc., increases the difficulty of mixing, reduces tensile strength, increases modulus, and decreases the resistance to cut growth. Polymers with significant gel content have reduced elastic memory (but lower shrinkage and lower surface roughness) and improved dimensional stability, two important qualities in extrusion and calendaring operation.

Vulcanization was discovered by Goodyear in 1839 (33). By incorporating elemental sulfur with natural rubber and heating the mass, he found that the resultant compound yielded a tough, elastic material, markedly different from the unvulcanized state. Modern rubber compounding (qv) has come a long way since the discovery of vulcanization, but its explanation still remains quite



theoretical (34). As a class, SBR is slower curing than natural rubber. This is thought to be caused by the lower unsaturation in SBR.

The art of compounding requires extensive experience and knowledge of the many compound ingredients. A typical rubber compound in addition to polymer contains one or more ingredients from the following general classes: vulcanizing agents, accelerators, accelerator activators, antioxidants, pigments, and softeners (see RUBBER CHEMICALS) (35).

The vulcanizing agent, which supplies the bridge between the polymer chains, is still furnished predominantly by the sulfur molecule in commercial formulations. Peroxide vulcanizers that produce carbon-to-carbon cross-links are also important. Thiuram disulfides are used in special applications, such as improved heat resistance. Other agents are of more academic interest.

Accelerators are chemical compounds that increase the rate of cure and improve the physical properties of the compound. As a class, they are as important as the vulcanizing agent itself. Without the accelerator, curing requires hours or even days to achieve acceptable levels. Aldehyde amines, thiocarbamates, thiuram sulfides, guanidines, and thiazoles are all classified as accelerators. By far, the most widely used are the thiazoles, represented by mercaptobenzothiazole (MBT) and benzothiazyl disulfide (MBTS).

Accelerator activators are chemicals required to initiate the acceleration of the curing process. They also improve the polymer compound quality. This class includes zinc oxide (pure) and stearic acid. Other compounds that have been in use are litharge, magnesium oxide, amines, and amine soaps.

Antioxidants (qv) are routinely added to the compounds over and above those contained in the polymer at manufacture. Finished products are subjected to a wide variety of activities causing degradation. Molecules with the propensity to neutralize free radicals by destruction, absorption, or disproportionation can accomplish this phenomenon in different ways. Incorporation of two or more different chemical categories often enhances protection much better (synergism) than the use of higher levels of individual additives. The most popular chemical classes shown to have good antioxidant properties are phenols, phosphites, thioesters, and amines. Because many antioxidant compounds are highly colored, they may tint the finished article. Amines and quinolines have the propensity to stain, that is, to transfer some of the color they impart from the compound in which they are used to a surface in contact with that compound, and are classified as stainers. These characteristics must be kept in mind when choosing the antioxidant system.

Antiozonants (qv) prevent or reduce polymer degradation by the active ozone molecule. Some antioxidant compounds, such as the *para*-phenylene-diamines, are excellent as antiozonants (36). The protection by these compounds is thought to be either a reaction with the ozone before it can react with the surface of the rubber or an aid in reuniting chains severed by ozone (37).

Pigments (qv) improve or change polymer properties as well as lower product costs. Reinforcement of SBR by carbon blacks allows this family of polymers to compete with natural rubber (see CARBON, CARBON BLACK). It is the most important attribute of the pigment in SBR processing. Two other important groups of pigments are the silicates and silicas. Other materials such as zinc oxide, clays, and calcium carbonate act more as inert fillers to lower the overall compound

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cost rather than to impart reinforcement. Softeners, ie, plasticizers, reinforcing agents, extenders, lubricants, tackifiers, and dispersing aids, are used as processing aids to enhance mixing of uncured stocks and soften cured compounds.

SBR rubber compounds are prepared in two stages: the nonproductive and the productive phases. In the nonproductive phase the compound ingredients are mixed, usually in internal mixers (Banbury). The mixing time is usually short and the compound temperature is in the 160–195°C range. This stock is discharged from the mixer to equipment that allows cooling and a convenient storage form, such as a mill or an extruder/die plate that yields a sheet or pelletized form. Usually the material is coated with a slurry of clay, calcium carbonate, or zinc stearate to prevent self-adhesion.

The productive stock, ie, the curable compound, is made up by mixing the nonproductive stock in the Banbury once more with the curative package (sulfur, accelerators, etc). This time the drop temperature is lower, in the range of 95–112°C. The productive stock is then sheeted or pelletized and coated with the dip coat, cooled, and finally stored, ready for further processing for final fabrication.

Economic Aspects and Uses

Styrene-butadiene elastomers, emulsion and solution types combined, are reported to be the largest-volume synthetic rubber, with 28.7% of the world consumption of all synthetic rubber in 1994 (38). This percentage has decreased steadily since 1973 when SBR's market share was 57% (39). The decline has been attributed to the switch to radial tires (longer milage) and the growth of other synthetic polymers, such as polyethylene, polypropylene, polyester, and polystyrene. Since 1985, production of SBR has been flat (Table 3).

Worldwide long-term consumption of SBR is projected to increase 2.5% per year through 1999 (Table 4). SBR is forecast to remain the dominant elastomer of

Table 3. Synthetic Rubber Production^{a,b}, 10³t

Type ^c	1985	1990	1992	1994	% Change. 1993/1994
SBR					
solid	2284	2398	2358	2433	5.0
latex ^d	289	264	300	299	-2.2
polybutadiene elastomer (BR)	978	1164	1264	1452	5.9
polyisoprene rubber (IR)	110	142	115	111	16.8
chloroprene rubber (CR)	321	306	260	276	15.0
ethylene propylene diene monomer (EPDM)	453	622	617	672	11.3
nitrile rubber (NBR)	213	246	255	277	9.1
others	563	574	606	543 ^e	-11.3
<i>Total</i>	<i>5211</i>	<i>5716</i>	<i>5775</i>	<i>6063^e</i>	<i>4.5</i>

^aRef. 40. ^bExcludes Central Europe, Socialist Countries of Asia, CIS. ^cFor all polymers latices are included, except for SBR where they are shown separately. ^dExcludes carboxylated latices. ^eThe change reflects a change in the International Institute of Synthetic Rubber Producers (IISRP) reporting base; growth rates not available in 1994.

Table 4. Worldwide Long-Term New Rubber Consumption By Elastomer Type^a, 10³ t

Elastomer	1994	1995 ^b	1999 ^b
SBR			
solid	2,589	2,774	3,085
latex	400	413	467
carboxylated SBR latex	1,473	1,509	1,670
polybutadiene	1,427	1,541	1,726
ethylene propylene diene monomer (EPDM)	653	679	750
chloroprene rubber (CR)	252	258	293
nitrile rubber (NBR)	319	337	391
other synthetics ^c	1,176	1,369	1,549
<i>Total Central Europe SR</i>	250	268	351
<i>Total Asia CPEC SR</i>	485	519	680
<i>Total synthetics</i>	9,022	9,666	10,962
natural rubber	5,425	5,595	6,264
<i>Total new rubber</i>	14,447	15,289	17,226
synthetic, %	62.4	63.2	63.6

^aRef. 40.^b1995 and 1999 values are forecast.^cIncludes isoprene-isobutyl rubber (IIR), polyisoprene rubber (IR), and other synthetic rubbers (SR).**Table 5. Worldwide Long-Term New Rubber Consumption By Area and Type^a, 10³ t**

Elastomer	Western Europe			North America		
	1994 ^b	1995 ^c	1999 ^c	1994 ^b	1995 ^c	1999 ^c
SBR						
solid	568	586	620	852	860	883
latex ^d	125	125	125	79	80	83
carboxylated SBR	570	584	645	634	646	699
polybutadiene elastomer (BR)	280	288	312	500	507	510
ethylene propylene diene monomer (EPDM)	225	236	266	264	270	274
chloroprene rubber (CR)	66	66	67	76	77	79
nitrile rubber (NBR) (solid and latex)	89	92	100	122	124	125
other synthetics ^c	241	251	278	408	420	426
<i>Total synthetic rubber</i>	2164	2228	2413	2935	2984	3080
natural rubber	900	930	1010	1106	1111	1103
<i>Total new rubber</i>	3064	3159	3423	4041	4094	4183
synthetic, %	70.6	70.5	70.5	72.6	72.9	73.6
thermoplastic elastomer (TPE)	299	314	371	358	387	496

^aRef. 40.^bEstimated December 1994.^cForecast prepared during first quarter of 1995.^dNoncarboxylated.^eIncludes isoprene-isobutyl rubber (IIR), polyisoprene rubber (IR), and others.

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2.9 73.6
17 496

all synthetic polymers in the same time frame. In 1993, use of SBR encompassed the following: tires and tire-related products, including tread rubber, 80%; mechanical goods, 11%; other automotive uses, 6%; and adhesives, chewing gum base, shoe products, flooring, etc, for the remaining 3% (41).

North America has led the world in consumption of SBR and will continue for the rest of the twentieth century. As shown in Table 5, total demand for SBR, including emulsion (solid) and solution (solid), was 852,000 metric tons in 1994, up from 811,000 metric tons in 1993. Since the early 1990s growth has averaged about 3.2% per year. Projected growth in the near future, based on the tight supply of natural rubber, is 4–5%, through 1999.

Health and Safety Factors

Air quality and plant effluent have been monitored and more or less regulated from the inception of SBR manufacture. Between the 1970s and 1990s, regulatory restrictions on plant operations have increased significantly. The ever-decreasing limits on exposure levels include styrene and butadiene monomers as well as their dimers and by-products. Most local and state governments have strict discharge permits that limit what kind of chemicals and how much of it can be emitted into the environment.

The American Conference of Governmental Industrial Hygienists (ACGIH) has set a time-weighted average (TWA) of 50 ppm for styrene monomer (42). For butadiene monomer, ACGIH has set the exposure limit of TWA at 10 ppm (43). As of this writing (1996), the Occupational Safety and Health Administration

Table 5. (Continued)

Asia and Oceania			Africa and Middle East		
1994 ^b	1995 ^c	1999 ^c	1994 ^b	1995 ^c	1999 ^c
684	714	832	60.7	63.2	71.5
141	146	164	4.0	4.1	6.0
231	241	280			
445	464	540	28.0	28.7	31.5
141	146	165	5.0	5.3	7.0
84	87	101	6.0	6.1	6.5
77	80	94	3.2	3.2	3.7
217	227	267	21.0	21.8	25.0
2020	2105	2443	127.9	132.5	151.3
2070	2120	2340	188.0	194.9	215.2
4090	4224	4783	315.8	327.4	366.5
49.4	49.8	51.0	40.5	40.5	41.3
148	154	179	5.5	5.9	7.7

(OSHA) is reviewing their TWA, which is set at 1000 ppm for butadiene. It is likely that the new TWA will be set at 1 or 2 ppm. Both styrene and butadiene are considered suspect carcinogens.

Title V of the Clean Air Act Amendments of 1990 covers federally approved state operating permits for manufacturing facilities. One requirement of this regulation is that manufacturers must report emissions information of identified hazardous air pollutants specific to their operation from a list of 189 named in the Clean Air Act Amendments. Rubber and tire manufacturers had to meet this requirement by the end of 1995. The Rubber Manufacturers Association has begun an industrywide project to develop accurate and reliable emissions data to aid manufacturers to comply with these requirements (44).

In 1988, the German government issued technical regulation for hazardous materials, TRGS 552. Among other things, 12 volatile nitrosamines were specified and an orientation value of $2.5 \mu\text{g}/\text{m}^3$ was set for the rubber industry. In 1992 the regulation was redefined. The following levels/action are being enforced in Germany: (1) up to $0.1 \mu\text{g}/\text{m}^3$ constitutes no exposure; (2) if levels exceed $0.25 \mu\text{g}/\text{m}^3$, action needs to be taken; (3) if level exceeds $0.65 \mu\text{g}/\text{m}^3$, respirators and medical monitoring must be offered; and (4) if levels exceed $1.00 \mu\text{g}/\text{m}^3$, respirators are mandatory.

This regulation is only concerned with volatile nitrosamines in the workplace air. A principal problem in enforcement is in the detection method. Only certain analytical laboratories are certified and reproducibility is difficult to achieve. Epidemiological studies have shown volatile nitrosamines to be carcinogenic in animals (45). Volatile nitrosamines are formed when secondary amine compounds break down and are nitrosated. In rubber this occurs primarily during the vulcanization stage, where accelerators, which are predominantly secondary amine compounds, decompose, forming lower molecular weight compounds, and are nitrosated either from oxides of nitrogen in the air or from nitrate-nitrite salts in the vulcanization process. Other sources of these secondary amines are as contaminants in compounding ingredients and as trace amounts in emulsion SBR, from the residue of certain shortstopping chemicals used in its manufacture.

There is an industry trend to supply SBR certifiably free of volatile nitrosamines or nitrosatable compounds. This has generally been accomplished by replacing shortstop systems based on carbamates and hydroxyl amines with products that are not based on secondary amines or are secondary amines of high molecular weight, such as dibenzylthiocarbamate. A more recently issued patent for ESBR shortstop is based on isopropylhydroxylamine, a primary amine that does not form nitrosamine (46).

Of primary concern to local, state, and federal governments is the growing stockpile of scrap tires. It was estimated by the Rubber Manufacturer's Association that for the year 1994, 242 million tires were added to the staggering number stockpiled haphazardly throughout the United States. The threat of huge piles of scrap tires catching fire is cited as a principal concern. Past experience has shown how such fires pollute the air and threaten groundwater as the large quantities of oil released in the incomplete burning become a serious runoff problem. In 1991 the federal government instituted the Intermodal Surface Transportation Act, which, among other things, mandates the use of ground rubber

from scrap by most states. Money to encourage this technology to increase use has been allocated (see RECYC).

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from scrap tires in asphalt paving. Being an unfunded mandate, it was ignored by most states and the Federal Highway Administration has not been authorized money to enforce this provision (47). There is heated debate on whether or not this technology is in fact worthwhile (48). Although use of scrap tires is projected to increase rapidly in the next three to five years, the only economically feasible use has been as a fuel or fuel supplement in utility and industrial applications (see RECYCLING, RUBBER) (49).

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STYRENE-BUTADIENE SOLUTION COPOLYMERS. See
ELASTOMERS, SYNTHETIC.

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CONCISE ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

Jacqueline I. Kroschwitz, *Executive Editor*



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BUTADIENE POLYMERS

Production of elastomers and plastics consumes by far the largest amount of butadiene monomer. Among the elastomers, the most important synthetic rubber and still most widely used rubber in the world, is the copolymer SBR (styrene-butadiene rubber). The butadiene-acrylonitrile copolymer (nitrile rubber or NBR) has widespread use where solvent and oil resistance are desired. Homopolymers of polybutadiene are widely used in tire tread and sidewall compounds and are important as impact modifiers in HIPS (high impact polystyrene) and ABS (acrylonitrile-butadiene-styrene) resins (see ACRYLONITRILE-BUTADIENE-STYRENE POLYMERS). Block copolymers (qv), such as SBS (styrene-butadiene-styrene) are important as adhesives (see ADHESIVE COMPOSITIONS). In addition, butadiene is the starting material for the preparation of hexamethylenediamine, a component of nylon-6,6.

Butadiene Monomer

Molecular Structure. 1,3-Butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, is the simplest conjugated diene. The cumulene isomer, 1,2-butadiene, $\text{CH}_3-\text{CH}=\text{C}=\text{CH}_2$, is commercially important only in molecular-weight control in the manufacture of butadiene rubbers.

The structure of 1,3-butadiene has received much theoretical attention because of its symmetry and simplicity. Heats of hydrogenation and combustion reveal that the stabilization contributed by the conjugation of the double bonds is 12.5–14.6 kJ/mol (3–3.5 kcal/mol). Electron diffraction revealed a planar molecule with bond angles $\text{C}=\text{C}-\text{C}$ 122.4° and $\text{C}=\text{C}-\text{H}$ 119.8°.

Physical Properties. At room temperature, 1,3-butadiene is a highly reactive, colorless gas with a mildly aromatic odor. Physical properties are given in Table 1.

Reactions. The chemistry of butadiene is prototypical of hydrocarbons containing conjugated double bonds. Butadiene is a reactive and versatile material. Reactions include self-condensations, Diels-Alder reactions, and addition reactions.

Manufacture. As world economics have changed since World War II, butadiene production has shifted from dehydrogenation of butane and butenes to by-product formation in ethylene manufacture.

Purification. Butadiene is produced from petroleum in a crude C_4 stream. For polymerization, butadiene that is at least 99 mol % pure is required. Alkynes are the most troublesome impurities. Separation of the butadiene from other C_4 products is also necessary. Simple fractional distillation is effective for removing the light (C_3) and heavy (C_5) ends from butadiene, but not for removing the various C_4 s because of the closeness of the boiling points to each other and to butadiene. Also, butadiene forms azeotropes with *n*-butane and 2-butene. The

Table 1. Physical and Thermodynamic Properties of Butadiene

Property	Value
molecular weight	54.09
boiling point, °C at 101.3 kPa ^a	-4.413
melting point, °C	-113
freezing point, in air at 101.3 kPa ^a , °C	-108.915
density, at saturation pressure at 20°C, g/mL	0.6211
pressure coefficient of boiling point at 101.3 kPa ^a , °C/Pa	4.502
vapor pressure of liquid at 21°C, kPa ^a	24.5
critical temperature, °C	152
critical pressure, MPa ^b	4.33
critical density, g/mL	0.245
critical volume, mL/g ^c	4.09
flash point, °C	-76.1

^a To convert kPa to mm Hg, multiply by 7.5.

^b To convert MPa to atmospheres, multiply by 9.87.

^c To convert mL/g to L/mol, multiply by 0.0540.

most widely used recovery systems are extraction with aqueous cuprous ammonium acetate (CAA) and solvent extractions with furfural, acetonitrile, dimethylformamide, dimethylacetamide, or *N*-methylpyrrolidinone.

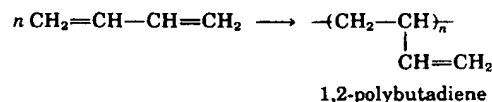
Health and Safety Factors. *Toxicity.* Butadiene causes tumors in male and female rats and should be considered a possible human carcinogen.

Handling and Storage. Butadiene is dangerous because of its explosiveness when mixed with air. Because of the high vapor pressure of the liquid, it must be kept under pressure.

Polymer Structure

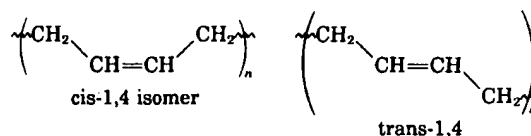
Microstructure (qv) refers to the disposition of the double bonds present in the polymer chain and macrostructure refers to long chain features such as extent of branching, molecular weight, and molecular-weight distributions.

Microstructure. Butadiene polymerizes by addition (see ADDITION POLYMERIZATION). Having two double bonds, it forms a variety of polymer structures. One of these, known as the vinyl or 1,2-type, results from addition across one of the double bonds:



Three vinyl structures are possible: the isotactic, the syndiotactic, and the heterotactic (or atactic).

A second structure arises by 1,4-addition when both double bonds participate. The remaining double bond in the polymer backbone permits two 1,4-structures, the *cis*-1,4 (or *Z*), and the *trans*-1,4 (or *E*) isomers. In the absence of side chains there is no tacticity.



In an actual polymer it is possible to have any or all of the several forms in a single chain. The structures indicated have all been synthesized individually, as well as in various mixtures, to give polymers with a preponderance of either 1,2- or 1,4-units.

Polymerization

Polymerization is either initiated or catalyzed and done in homogeneous solution, including bulk polymerization where excess monomer functions as the solvent, and in water emulsion. The propagating polymer may be an anion, cation, free-radical, or coordination complex. Ionic species and coordination species that are reactive enough to initiate polymerizations are usually too reactive to be stable in water solution, but free-radical polymerizations may be carried out in aqueous or non-aqueous media.

In contrast to homogeneous free-radical systems, emulsion polymerization (qv) affords high propagation rates and high molecular-weight products of elastomer quality. The propagating radical chains are somewhat physically isolated and thus prevented from recombining as rapidly as they would in solution or bulk media.

Styrene-Butadiene Copolymers. The synthetic rubber industry, based on the free-radical emulsion process, was created almost overnight during World War II. Styrene-butadiene rubber (SBR) created at that time gives such good tire treads that natural rubber has never regained this market. The free-radical emulsion process is still used today.

Commercial Grades. Table 2 gives trade names but covers only commercial grades of SBR and emulsion-type polybutadienes.

Table 2. Trade Names of SBR and Emulsion-type Polybutadienes

Trade name	Manufacturer
Ameripol	BFGoodrich
ASRC	American Synthetic Rubber Corp.
Buna	Buna Werke Huls G.m.b.H.
Copo	Copolymer Rubber and Chemical Corp.
Europrene, Intol, Sirel	Eoxo Chemical Ltd.
Gentro	The General Tire & Rubber Co.
JSR	Japan Synthetic Rubber Co.
Philprene	Phillips Chemical Co.
Pliofex	The Goodyear Tire & Rubber Co.
Polysar, Krylene, Krynol	Polysar, Ltd.
Sumitomo	Sumitomo Chemical Co.
Synpol	Synpol, Inc.

Acrylonitrile-Butadiene Copolymers (NBR). The generic term nitrile rubber refers to copolymers of any unsaturated nitrile and diene, but commercially are almost exclusively acrylonitrile and butadiene.

Nitrile rubbers are used primarily where resistance to swelling by oils and greases is required. A high nitrile content increases swell resistance but limits flexibility at low temperatures.

Nitrile rubbers are produced in emulsion. Manufacturers have their own trade names and code designations (Table 3).

Other Emulsion Copolymers. Many monomers have been copolymerized with butadiene. A few have some commercial util-

Table 3. Trade Names of Nitrile Rubbers

Trade name	Producer
Chemigum	The Goodyear Tire & Rubber Co.
Europrene	Eoxo Chemical Ltd.
Hycar	BFGoodrich Co.
Krynac	Polymer Corporation, Ltd.
Nysyn	Copolymer Rubber Co.
Paracril	Uniroyal Inc.
JSR	Japan Synthetic Rubber Co.
Elaprim	Montepolimeri S.P.A.
Perbunan	Bayer A.G.

ity. A butadiene-styrene-vinylpyridine terpolymer latex is used for improving tire cord and fabric adhesion to rubber.

Latex. The first latices (qv) were polymer mixtures stabilized with antioxidant. They contained 25–30% solids, but were soon succeeded by latex of higher solids content. Latex is useful for coatings, adhesives, paper treating, foam rubber, carpet backing, and dipped goods.

Anionic Polymerization. Microstructure. Changes in the recipe for free-radical polymerization, in emulsion, solution, or bulk, cause little or no change in the microstructure of the resultant polymers, whereas changes in the recipes for alkali metal polymerization often appreciably affect the structure of the product (see also ANIONIC POLYMERIZATION).

The structures of polybutadiene obtained in hydrocarbon media with alkali metal catalysts and in an emulsion are shown in Table 4.

Table 4. Microstructure of Alkali Metal-catalyzed Butadienes

Catalyst or condition	cis-1,4, %	trans-1,4, %	1,2, %
lithium	35	52	13
sodium	10	25	65
potassium	15	40	45
rubidium	7	31	62
cesium	6	35	59
emulsion	18	64	18

Lithium-initiated Butadiene Copolymers. In lithium-initiated systems, butadiene comonomers are limited to materials such as styrene and isoprene that do not undergo terminating side reactions with strong bases. The most useful comonomer is styrene. Because of the stability and "living" nature of the allylic lithium end group, butadiene-styrene copolymers of widely different structures and properties are conveniently prepared.

Block Copolymers. The utility of lithium-based anionic initiator systems is evident in the synthesis of block copolymers (qv). The living anionic end of a polymer chain A can initiate the polymerization of another monomer B to form an A-B block copolymer.

End-group Reactions. Anionic polymerization is primarily concerned with the anionic end of the polymer chain. With monofunctional initiators, termination of the polymerizing butadiene with various reagents can give rise to many polymers

Table 5. Characteristics of Crystalline Polybutadienes

Polybutadiene	Lattice	Monomers/ unit cell	Mp, °C	Crystal density, g/cm ³	Repeat distance, nm
1,4-trans, 99–100%	pseudo-hexagonal	1	145	0.97 (I) 0.93 (II)	0.485 0.465
1,4-cis, 98–99%	monoclinic	2	2	1.01	0.86
1,2-isotactic, 99%	rhombohedral	2	126	0.96	0.65
1,2-syndio- tactic, 98%	helical	3	156	0.96	0.514

containing an end-functional group. A diinitiator gives a polybutadiene with two live ends that can be terminated to give α,ω difunctional polymers. Although such polymers can be produced by oxidative degradation or free-radical polymerization by an initiator containing a functional group, this technique gives better control.

Transition-metal Catalysts. Transition-metal or coordination catalysts (ie, Ziegler-Natta catalysts (qv)) comprise mixtures of an organometallic and a transition-metal compound. These catalysts often contain a heterogeneous, insoluble phase, which may be a complex of the two components. The combination of two or more ingredients permits a wide range of activities and structures and has led to unusual, new polyolefins and polydienes including high *cis*-1,4-polyisoprene, which duplicates natural rubber, *Hevea brasiliensis* (see also ISOPRENE POLYMERS). Among polymers not found in nature, high *cis*-1,4-polybutadienes have attained commercial importance.

The transition-metal catalysts that promote *cis*-addition fall into three classes: titanium-based catalysts containing iodine and trialkylaluminums, cobalt-based catalysts containing alkylaluminum halides, and nickel-based catalysts containing BF₃ and trialkylaluminums. Recently, rare-earth catalysts, particularly those based on neodymium, have shown commercial potential. Other catalysts allow the preparation of *trans*-1,4-polybutadiene and syndiotactic and isotactic 1,2-polybutadiene. Generally, π -allyl complexes of nickel, cobalt, titanium, and rhodium tend to produce 1,4-polybutadienes, whereas chromium, molybdenum, and palladium produce 1,2-polybutadienes.

Butadiene Copolymers. Using transition-metal catalysts, butadiene has been copolymerized with isoprene, 2,3-dimethylbutadiene, and styrene.

Cationic Polymerization. Cationic polymerization of butadiene is conducted at very low temperatures to reduce gel formation. Emulsion or solution polymerization of butadiene with rhodium salts gives 98 + % *trans* polymer and is thought to be cationic.

Polymer Properties

Uncured Polymers. Polybutadienes of the four possible structures have been prepared sufficiently pure for crystallization and structure determination (Table 5).

Cured Polymers. The microstructure of polybutadiene affects its mechanical behavior. Changes in physical properties occur as the structure approaches pure *cis* or pure *trans*; little change is evident between 25 and 80% *cis* content. High *cis* polymers have high resilience and low hysteresis. Very high *cis* (>96%)

polymers crystallize on being stretched and, like *Hevea*, the gum stocks have high tensile strengths. High *trans* polymers are crystalline with high tensile strength gum stock, high hysteresis, and inferior resilience. The amorphous polymers of high vinyl content (95% 1,2) have fairly good tensile properties, low hysteresis, and poor low-temperature characteristics; *T_g* is approximately 0°C. Crystalline, syndiotactic 1,2-polybutadiene (70% 1,2) resembles the amorphous polymer but has higher tensile strength and elastic modulus.

The widespread use of butadiene-based elastomers in automobile tires (qv) is attributable to their favorable balance of cost, processibility and resistance to heat, abrasion, and oxidative degradation.

Although nitrile rubbers swell more in polar solvents than nonpolar, they can be used with antifreeze solutions and in similar applications. They are also used in poly(vinyl chloride) and with styrene (ABS resins). In textiles and leather, nitrile latices are used to increase abrasion resistance and as binders for pigments. In paper manufacture they are used as pigment binders, coatings for increased waterproofing and grease-proofing, and in making high strength papers.

Processing

Elastomers, unlike fibers and plastics, require fillers (qv) and other ingredients as well as curing (qv). Processing involves three steps: mastication of the raw rubber with fillers, processing aids, curatives, antioxidants, etc; molding of the rubber compound into the desired shape; and cure (vulcanization) by heat. Similar equipment is used for butadiene polymers and other rubbers. Indeed, the commercial success of a new rubber often depends on whether it can be handled in existing equipment.

Economic Aspects

Butadiene consumption is dominated by the synthetic rubber industry, which in turn is dominated by the tire market. Ap-

Table 6. U.S. Production of Butadiene-type Rubbers, 10³ Metric Tons

Year	SBR	BR	N-Type
1952	666		13.9
1962	979		36.5
1972	1500	298	75
1977	1513	362	80
1979	1436	397	89
1981	1085	342	70
1982	876	288	45
1983	904	332	55

proximately 70% of U.S. butadiene consumption is used in rubber products, of which over 50% is for tires. Technological change and economic conditions greatly affect butadiene consumption. Production figures are shown in Table 6.

Prices. The approximate 1985 list prices of rubber are shown in Table 7.

Table 7. 1985 Rubber Prices^a

Rubber or monomer	\$/kg
butadiene monomer	0.73
SBR	
emulsion	1.23
anionic	1.25
cis-polybutadiene	1.47
nitrile rubber	2.33
natural rubber ^b	0.93

^a Actual prices may vary considerably because of discounting.

^b No. 1 RSS.

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BUTENE POLYMERS

Polybutylene (PB) refers to a series of commercial semicrystalline resins derived from high molecular-weight, predominantly isotactic poly(1-butene) homopolymer or copolymer. Poly(1-butene) can be represented by the formula $[-CH_2CH(C_2H_5)-]_n$, where n is the degree of polymerization. Unless otherwise indicated, the poly(1-butene) or PB in this article refers to isotactic homopolymer.

Properties of 1-Butene

1-Butene is a colorless gas with a boiling point of -6°C at 101.3 kPa (1 atm). 1-Butene undergoes isomerization, promoted by various catalysts, and hydrogenation. It undergoes Ziegler-Natta polymerization to form an isotactic, crystalline polymer. Cationic or free-radical initiators produce atactic poly(1-butene), which is amorphous (see also ZIEGLER-NATTA CATALYSTS).

Manufacture of 1-Butene

1-Butene is produced commercially, together with other α -olefins, by the catalytic oligomerization of ethylene.

Polymer Properties

Polymorphism. Poly(1-butene) exhibits polymorphism, including the crystal forms I (twinned hexagonal), II (tetragonal), III (orthorhombic), I' (untwinned hexagonal), and II'.

Melt Crystallization. Poly(1-butene) crystallizes from the unstrained melt in spherulitic morphology (qv). The crystallization rate increases with increasing molecular weight. The temperature for attaining homogeneous nucleation of poly(1-butene) crystallization is below 0°C , compared to ca 81°C for linear polyethylene and 88°C for isotactic polypropylene.

Transformation in the Solid State. The metastable form-II poly(1-butene), crystallized from the melt, undergoes a spontaneous, irreversible transformation to the stable form I. This transformation is affected by temperature, pressure, mechanical stress and orientation (qv), molecular weight, tacticity, comonomers, additives, impurities, sample thickness, and γ radiation.

Mechanical Properties. Generally, PB does not exhibit necking on elongation, but rather shows uniform sample deformation and strain-hardening. The yield strength, ultimate strength, and modulus increase with increasing crystallinity and decrease with increasing temperature. The glass-transition temperature (T_g) of poly(1-butene) ranges from -17 to -25°C . The activation energy for viscous flow is 45 kJ/mol (11 kcal/mol). The properties of pipe-grade PB are listed in Table 1.

Table 1. Properties of Pipe-grade Polybutylene Resin^a at 23°C

Property	ASTM test method	Value
melt index, g/10 min	D1238 ^b	0.4
density, g/cm ³	D792	0.93–0.94
tensile properties		
yield strength, MPa ^c	D638	16–18
break strength, MPa ^c	D638	32–35
elongation to break, %	D638	275–320
modulus, MPa ^c	D638	290–295
flexural modulus, MPa ^c	D790	375–380
notched Izod impact strength, J/m ^d	D256	640–800
hardness, Shore	D2240	D60
brittleness temperature, $^\circ\text{C}$	D746	-18
melting temperature, $^\circ\text{C}$	D3418	124–130
Vicat softening point, $^\circ\text{C}$	D1525	112–114
heat deflection temperature, $^\circ\text{C}$		
at 1.82 MPa ^c	D648	54–60
at 0.46 MPa ^c	D648	102–113
linear coefficient of thermal expansion, m/m/ $^\circ\text{C}$	D696	0.00013
thermal conductivity, W/(m·K)	C177	0.22
UL flammability	UL94	HB
dielectric constant, 10^3 – 10^6 Hz	D150	2.53
dissipation factor, 10^3 – 10^6 Hz	D150	0.0005
water absorption, in 24 h, %	D570	<0.03

^a Compression-molded into plaques and after transformation to stable form I.

^b Condition E.

^c To convert MPa to psi, multiply by 145.

^d To convert J/m to ft·lb/in., divide by 53.38.

^e To convert MPa to atm, divide by 0.101.

Chemical Properties. Polybutylene resins resist most acids and bases below 90°C and many chemicals, solvents, soaps, and detergents. Resistance is poor to strong oxidizing acids and to aromatic and chlorinated hydrocarbon solvents above 60°C . During thermooxidative and photooxidative degradation, PB generally undergoes chain scission rather than cross-linking. Stabilizers prevent oxidation induced by heat and ultraviolet radiation.

Solution Properties. At elevated temperatures, poly(1-butene) dissolves in benzene, toluene, decalin, tetralin, chloroform, and α -chloronaphthalene. Its solubility depends on temperature, molecular weight, and crystallinity.

Polymerization

Isotactic poly(1-butene) is manufactured by stereospecific Ziegler-Natta polymerization (qv).

Processing

PB is melt extruded to form pipe, sheet, or profile section. Conventional single-screw extrusion is used; vacuum- or pressure-sizing can be used for dimensional control in pipe manufacture. Film may be manufactured by the blown or cast process. Coextrusion and extrusion coating are also practiced. PB can also be injection molded. In melt processing of commercial PB resins, crystal forms II and I are generally encountered and the transitions must be considered in part design.

Economic Aspects

The 1986 worldwide PB market was approximately 11,200 t/yr. The bulk list price of PB resins ranges from \$1.84 to \$2.87/kg, depending on the grade.

Health and Safety Factors

1-Butene may be encountered when sealed containers are opened. The gas is flammable. It is not toxic at moderate concentration, but acts as an anesthetic and asphyxiant at higher concentration.

Uses

The most important commercial outlet for PB resins is in pipe, with applications that include hot- and cold-water plumbing

and cold-water service. PB is also used in specialty films and film coats for packaging dry foods, meats, and medical parts. Sheet is used for abrasion-resistant lining applications. PB resins are injection molded into fusion fittings for pipe and tubing. Other uses are in adhesives and sealants formulations and as a modifying additive with other polyolefins.

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BUTYLENE POLYMERS. See BUTENE POLYMERS.

BUTYL METHACRYLATE POLYMERS. See ACRYLIC AND METHACRYLIC ESTER POLYMERS.

BUTYL RUBBER. See ISOBUTYLENE POLYMERS.

BUTYRATE PLASTIC. See CELLULOSE ESTERS, ORGANIC.

Synthetic rubber

From Wikipedia, the free encyclopedia

Synthetic rubber is a type of artificially-made polymer material which acts as an elastomer. An elastomer is a material with the mechanical (or material) property that it can undergo much more elastic deformation under stress than most materials and still return to its previous size without permanent deformation. Synthetic rubber serves as a substitute for natural rubber in many cases, especially when improved material properties are needed.

Natural rubber coming from latex is mostly polymerized isoprene with a small percentage of impurities in it. This will limit the range of properties available to it. Also, there are limitations on the proportions of *cis* and *trans* double bonds resulting from methods of polymerizing natural latex. This also limits the range of properties available to natural rubber, although addition of sulfur and vulcanization are used to improve the properties.

However, synthetic rubber can be made from the polymerization of a variety of monomers including isoprene (2-methyl-1,3-butadiene), 1,3-butadiene, chloroprene (2-chloro-1,3-butadiene), and isobutylene (methylpropene) with a small percentage of isoprene for cross-linking. Furthermore, these and other monomers can be mixed in various desirable proportions to be copolymerized for a wide range of physical, mechanical, and chemical properties. The monomers can be produced pure and addition of impurities or additives can be controlled by design to give optimal properties. Polymerization of pure monomers can be better controlled to give a desired proportion of *cis* and *trans* double bonds.

An urgent need for synthetic rubber that is derived from widely distributed feedstocks grew out of the expanded use of motor vehicles, and particularly motor vehicle tires, starting in the 1890s. Political problems that resulted from great fluctuations in the cost of natural rubber led to enactment of the Stevenson Act in 1921. This act essentially created a cartel which supported rubber prices by regulating production (see OPEC). By 1925 the price of natural rubber had increased to the point that companies such as DuPont were exploring methods of producing synthetic rubber to compete with natural rubber. In the case of Dupont the effort lead to the discovery of Neoprene which is a synthetic rubber that is too expensive to be used in tires, but has some very desirable properties that make it possible to use rubber in applications that would be unsuitable for natural rubber.

See also:

- Butyl rubber
- Styrene-butadiene
- Elmer Keiser Bolton

Uses of Synthetic Rubber

- molded: plumbing fixture; gaskets; hose; mechanical seal; mechanical belt; solid rocket propellant; tires
 - extruded: garden hose; inner tube; laboratory tubing
- sheet: Rigid-hulled inflatable boat; diving suit; glove; sleepsack; Knee high boots; protective clothing; radar absorbent material
 - die cut sheet
- foam: wetsuit; diveskin; glove; balaclava; wetsock; mousepad; orthopedic brace

- adhesive: adhesive tape; Liquid adhesive

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Categories: Polymers | Organic polymers

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ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

FOURTH EDITION

VOLUME **22**

SILICON COMPOUNDS
TO
SUCCINIC ACID AND SUCCINIC ANHYDRIDE



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polymer, which is difficult to fabricate because of its high melt viscosity, is more brittle than PS but can be toughened with rubber.

Some polymers from styrene derivatives seem to meet specific market demands and to have the potential to become commercially significant materials. For example, monomeric chlorostyrene is useful in glass-reinforced polyester recipes because it polymerizes several times as fast as styrene (61). Poly(sodium styrenesulfonate) [9003-59-2], a versatile water-soluble polymer, is used in water-pollution control and as a general flocculant (see WATER, INDUSTRIAL WATER TREATMENT; FLOCCULATING AGENTS) (63,64). Poly(vinylbenzyl ammonium chloride) [70504-37-9] has been useful as an electroconductive resin (see ELECTRICALLY CONDUCTIVE POLYMERS) (65).

Rubber-Modified Polystyrene. Rubber is incorporated into PS primarily to impart toughness. The resulting materials, commonly called high impact polystyrene (HIPS), are available in many different varieties. In rubber-modified PS, the rubber is dispersed in the PS matrix in the form of discrete particles. The mechanism of rubber particle formation and rubber reinforcement, as well as several reviews of HIPS and other heterogeneous polymers, have been published (21,22,66-70). The photomicrographs in Figure 5 show the different morphologies possible in HIPS materials prepared using various types of rubbers (71,72). If the particles are much larger than 5-10 micrometers, poor surface appearance of moldings, extrusions, and vacuum-formed parts are usually noted. Although most commercial HIPSs contain ca 3-10 wt % polybutadiene or styrene-butadiene copolymer rubber, the presence of PS occlusions within the rubber particles gives rise to a 10-40% volume fraction of the reinforcing rubber phase (22,73). Accordingly, a significant portion of the PS matrix is filled with rubber particles. Techniques have been published for evaluating the morphology of HIPS (72,74,75).

For effective toughening of otherwise brittle PS with rubbers, the following generalizations can be made. In order to have good impact strength over a wide temperature range, the T_g of the rubber must be below -50°C , as measured, eg. by torsion pendulum at 1 Hz. The use of butadiene rubbers is particularly effective when the rubber is present during the polymerization of styrene. Grafting of some styrene to rubber takes place, and occlusion of PS extends the volume fraction of the dispersed, reinforcing rubber phase. The rubber phase in the final product is cross-linked to some degree for the most effective reinforcement. Because the rubber phase exists in the form of discrete rubber particles, the degree of cross-linking does not significantly influence the melt flow, which is that of a linear, ie, uncross-linked, thermoplastic polymer. A variation in the degree of cross-linking may be needed to optimize product properties for different applications. Depending on the process and rubber concentration used, there is some latitude in the size of the rubber particles that results in a good balance of properties. This range may extend from <1 to $>5 \mu\text{m}$.

Rubber-Modified Copolymers. Acrylonitrile-butadiene-styrene polymers have become important commercial products since the mid-1950s. The development and properties of ABS polymers have been discussed in detail (76) (see ACRYLONITRILE POLYMERS). ABS polymers, like HIPS, are two-phase systems in which the elastomer component is dispersed in the rigid SAN copolymer matrix. The electron photomicrographs in Figure 6 show the difference in morphology

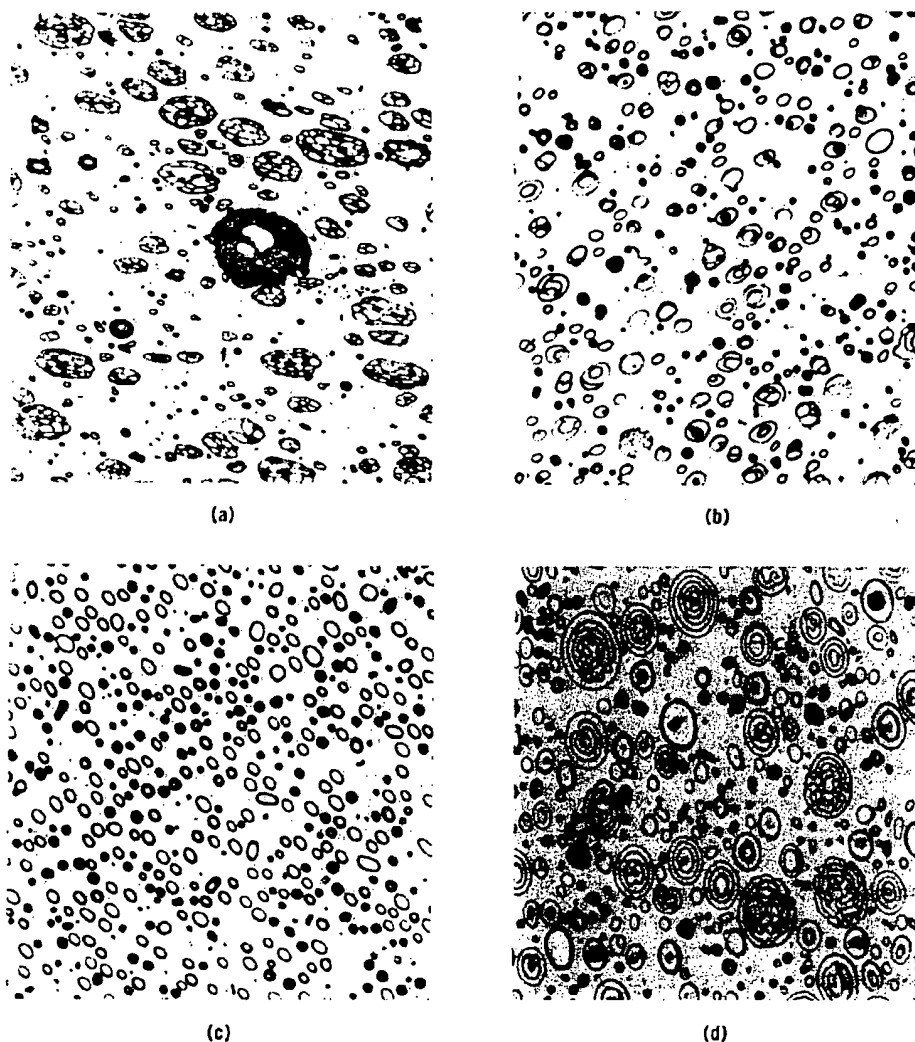


Fig. 5. Electron photomicrographs of several HIPS resins prepared using different types of rubbers.

of mass vs emulsion ABS polymers. The differences in structure of the dispersed phases are primarily a result of differences in production processes, types of rubber used, and variation in rubber concentrations.

Because of the possible changes in the nature and concentration of the rubber phase, a wide range of ABS polymers is available. Generally, they are rigid, showing a modulus at room temperature of 1.8–2.6 GPa ($(2.6-3.8) \times 10^5$ psi), and have excellent notched impact strength at room temperature, ca 135–4.00 J/m (2.5–7.5 ft lb/in.), and at lower (eg, -40°C) temperatures, 50–140 J/m (0.94–2.6 ft lb/in.). This combination of stiffness, impact strength, and solvent resistance makes ABS polymers particularly suitable for demanding applications. Another important attribute of several ABS polymers is their

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CONCISE ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

Jacqueline I. Kroschwitz, *Executive Editor*



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significant problem, because low temperatures are necessary to obtain high molecular weight. The polarity of the solvent plays a role in solvating the ion pair and, in general, the greater the dielectric constant of the solvent, the greater the rate of polymerization and the higher the molecular weight of the polymer.

Chain Transfer. Chain-transfer reactions are common and difficult to control in cationic polymerization of styrene, making molecular weight difficult to control. Although transfer to polymer and solvent are known to occur, chain transfer to monomer is the most important mechanism in cationic styrene polymerization.

Living Systems. A living carbocationic polymerization for styrene has been described. The chemistry involves the reaction of an organic acetate with BCl_3 and styrene at about -30°C in chloromethane.

Coordination Polymerization

Styrene monomer can also be polymerized to stereoregular structures through the proper use of coordination catalysts. Until recently, only isotactic polystyrene had been described (see INSERTION POLYMERIZATION; STEREOREGULAR LINEAR POLYMERS). More recently the preparation of syndiotactic polystyrene has also been discovered. Syndiotactic polystyrene is prepared with homogeneous coordination catalysts (see STEREOREGULAR STYRENE POLYMERS). Highly isotactic polystyrene is prepared using heterogeneous catalysts obtained from the reaction of aluminum alkyls with titanium chlorides.

The syndiotactic polymer has a melting point of about 270°C with a glass-transition temperature for the amorphous phase at about 100°C . Isotactic polystyrene melts at about 220 – 230°C . The crystallization rate for syndiotactic polystyrene also appears to be much greater than that of the isotactic material, which may give it more commercial potential.

Copolymerization

The variety of copolymers that can be prepared with styrene have greatly expanded the use of the monomer. Dramatic improvements or modifications of physical properties can be achieved by choosing the right comonomer. Table 1 lists reactivity ratios for typical styrene comonomers. A more extensive list has been published.

The reactivity ratios define the composition of the copolymer that is instantaneously produced from a monomer mixture. This is true in either a batch reactor or a continuous stirred-tank reactor. However, in the batch reactor, the copolymer composition drifts from that produced by the initial monomer composition to that produced by the monomer composition at the end of the reaction. In the ideal continuous stirred-tank reactor, all copolymer produced is of the same composition,

which is determined by the ratio of the unreacted monomers. Homogeneity in a continuous reactor system is controlled by the intensity of mixing and the number and location of addition points for the more reactive monomer (see COPOLYMERIZATION).

Copolymers of styrene include styrene-co-acrylonitrile (SAN), styrene-co-methyl methacrylate (SMMA), styrene-co-butadiene (SB), acrylonitrile-butadiene-styrene (ABS), styrene-co-maleic anhydride (SMA), styrene-co-divinylbenzene, and styrene-co- α -methylstyrene (SAMS).

Rubber-modified Polystyrene. Rubber is incorporated with polystyrene in commercial high impact polystyrene (HIPS). In order to provide a rubber with better compatibility with the continuous polystyrene phase, it is advantageous to graft the rubber with polystyrene. The most common commercial rubbers are pure polybutadiene or copolymers with styrene; *cis*-polybutadiene is particularly popular. Ethylene-propylene-diene terpolymer (EPDM rubber) is used to prepare impact-resistant polymers that are resistant to outdoor aging (see ETHYLENE-PROPYLENE ELASTOMERS).

In mass-produced rubber-modified polystyrene, the rubber is dissolved in the styrene. As the polymerization of the styrene proceeds, two phases are formed: a rubber-rich phase and a polystyrene-rich phase. Grafting occurs during the polymerization of styrene when some of the free radicals react with the rubber (see GRAFT COPOLYMERS). Grafting is important because the graft copolymer concentrates at the interface and strongly affects particle size, morphology, and toughness.

Commercial Processes

As with most polymeric materials, process and product considerations for polystyrene are intimately related. The choice and evolution of processes and range of possible operating conditions all weigh heavily on the quality, cost, and range of products that can be produced. Process evolution is closely tied to the capabilities of producing a wide range of products with useful combinations of properties at minimum cost.

Although polystyrene can be produced by free-radical, anionic, cationic, and Ziegler mechanisms, only the free-radical process is of major commercial interest. Anionic polymerization of styrene is limited to the production of narrow molecular weight distribution polystyrenes in laboratory quantities. These polymers are used for instrument calibration and theoretical studies of properties as functions of molecular weight. The anionic polymerization process is used commercially only for block copolymers of styrene with butadiene. Cationic polymerization is only used to produce low molecular weight polystyrenes for coatings and glues. All commercial molding and extrusion resins have weight-average molecular weights between 100,000 and 400,000 and distribution indexes (M_w/M_n) between 2 and 4. This range of molecular weights can be produced

Table 1. Styrene Comonomer Reactivity Ratios^a

Monomer 2	r_1^b	r_2^c	Temperature, $^\circ\text{C}$
acrylonitrile	0.4	0.04	60
butadiene	0.5	1.40	50
maleic anhydride	0.014	0.0	80
methyl methacrylate	0.52	0.46	60
<i>m</i> -divinylbenzene	0.65	0.60	60

^a Styrene is monomer 1.

^b $r_1 = k_{11}/k_{12}$.

^c $r_2 = k_{22}/k_{21}$.

Category:Organic polymers

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Subcategories

There are 5 subcategories to this category.

C

- Cellulose derivates

G

- Glycosaminoglycans

P

- Plastics
- Polyols
- Polysaccharides

Pages in category "Organic polymers"

There are 96 pages in this section of this category.

A

- Acrylonitrile butadiene styrene
- Agar
- Alginic acid
- Alkyd

B

- Butyl rubber

C

- CR-39
- Carbomers
- Catalin
- Celluloid
- Chlorinated polyvinyl chloride
- Cyamelide

D

P cont.

- PLGA
- Parkesine
- Phenol formaldehyde resin
- Phenolic resin
- Plastic bending
- Poly vinyl pyrrolidone
- Poly(3,4-ethylenedioxythiophene)
- Poly(p-phenylene oxide)
- Poly(p-phenylene sulfide)
- Poly(p-phenylene vinylene)
- Polyacetylene
- Polyacrylamide
- Polyacrylonitrile
- Polyaniline
- Polybutadiene
- Polybutylene terephthalate
- Polycaprolactone
- Polydiacetylenes
- Polydimethylsiloxane
- Polydioxanone
- Polyester
- Polyethylene

P cont.

- Polyoxymethylene
- Polyphthalamide
- Polypropylene
- Polypropylene glycol
- Polypyrrole
- Polysaccharide
- Polystyrene
- Polysulfone
- Polyurea
- Polyurethane
- Polyvinyl acetate
- Polyvinyl alcohol
- Polyvinyl chloride
- Polyvinylidene fluoride

R

- Rayon
- Rubber

S

- E**
- Dyneema
 - ECTFE
 - ETFE
 - Epoxy
- F**
- Fluoropolymer
- G**
- Galactomannan
 - Glycerine phthalate
 - GoldFlex
- H**
- High density polyethylene
 - Hydroxyl-terminated polybutadiene
- K**
- Kevlar
- L**
- Lignin
 - Linear low density polyethylene
 - Low density polyethylene
- M**
- Melanin
 - Memory foam
- N**
- Nitrocellulose
 - Nylon
- P**
- PEDOT:PSS
- Polyethylene amine
 - Polyethylene glycol
 - Polyethylene naphthalate
 - Polyethylene terephthalate
 - Polyglycolide
 - Polyhydroxybutyrate
 - Polyimide
 - Polyketone
 - Polylactic acid
 - Polymethyl methacrylate
 - Polyol
- Semi-flexible rod polymer
 - Sodium poly(aspartate)
 - Spandex
 - Spider silk
 - Styrene-butadiene
 - Synthetic rubber
- T**
- Tannin
 - Tholin
 - Triacetate
 - Tyvek
- U**
- Ultra high molecular weight polyethylene
 - User:J.Steinbock/Polyethylene
- V**
- Vectran
 - Viton
- Z**
- Zylon

- PEEK
- PEX

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Categories: Organic compounds | Polymers

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Polystyrene

From Wikipedia, the free encyclopedia

***Styrofoam** redirects here. For the music band of the same name see **Styrofoam (artist)**.*

Polystyrene is a polymer made from the monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum. At room temperature, polystyrene is normally a solid thermoplastic, but can be melted at higher temperature for molding or extrusion, then resolidified. Styrene is an aromatic monomer, and polystyrene is an aromatic polymer.

Polystyrene was accidentally discovered in 1839 by Eduard Simon, an apothecary in Berlin, Germany. From storax, the resin of *Liquidambar orientalis*, he distilled an oily substance, a monomer which he named styrol. Several days later Simon found that the styrol had thickened, presumably due to oxidation, into a jelly he dubbed styrol

oxide ("Stryroloxyd"). By 1845 English chemist John Blyth and German chemist August Wilhelm von Hofmann showed that the same transformation of styrol took place in the absence of oxygen. They called their substance metastyrol. Analysis later showed that it was chemically identical to Styroloxyd. In 1866 Marcelin Berthelot correctly identified the formation of metastyrol from styrol as a polymerization process. About 80 years went by before it was realized that heating of styrol starts a chain reaction which produces macromolecules, following the thesis of German organic chemist Hermann Staudinger (1881 - 1965). This eventually led to the substance receiving its present name, polystyrene. The I.G. Farben company began manufacturing polystyrene in Ludwigshafen, Germany, about 1931, hoping it would be a suitable replacement for die cast zinc in many applications. Success was achieved when they developed a reactor vessel that extruded polystyrene through a heated tube and cutter, producing polystyrene in pellet form.

Pure solid polystyrene is a colorless, hard plastic with limited flexibility. It can be cast into molds with fine detail. Polystyrene can be transparent or can be made to take on various colors. It is economical and is used for producing plastic model assembly kits, plastic cutlery, CD "jewel" cases, and many other objects where a fairly rigid, economical plastic of any of various colors is desired.

Polystyrene

Density	1050 kg/m ³
Electrical conductivity(σ)	10 ⁻¹⁶ S/m
Thermal conductivity	0.08 W/(m·K)
Young's modulus(E)	3000-3600 MPa
Tensile strength(σ_t)	46-60 MPa
Elongation @ break notch test	3-4%
Glass temperature	95 °C
melting point	-
Vicat B ^{<1>} (http://en.wikipedia.org/wiki/Polystyrene#endnote_)	90 °C
heat transfer coefficient (λ)	0.17 W/(m·K)
linear expansion coefficient (α)	8 10 ⁻⁵ /K
Specific heat (c)	1.3 kJ/(kg·K)
Water absorption (ASTM)	0.03-0.1
# ↑ Deformation temperature at 10 kN needle load	
source: A.K. van der Vegt & L.E. Govaert, <i>Polymeren, van keten tot kunststof</i> , ISBN 90-407-2388-5	

Contents

- 1 Standard bulk form
- 2 Solid foam
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- 4 Toughening
- 5 Cutting and shaping
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- 7 See also
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Standard bulk form

For architectural and engineering modelling, polystyrene is extruded into forms of standard modelling scale with the cross-sections of a miniature I-beam as well as rods and tubes. It is also formed into sheets with various patterns for this purpose as well. The blank sheets of polystyrene are referred to as "plasticard" in Britain, after the vulgarization of a trademark, but are called "sheet styrene" in the US.

Polystyrene fabricated into a sheet can be stamped (formed) into economic, disposable cups, glasses, bowls, lids, and other items, especially when high strength, durability, and heat resistance are not essential. A thin layer of transparent polystyrene is often used as an infra-red spectroscopy standard.

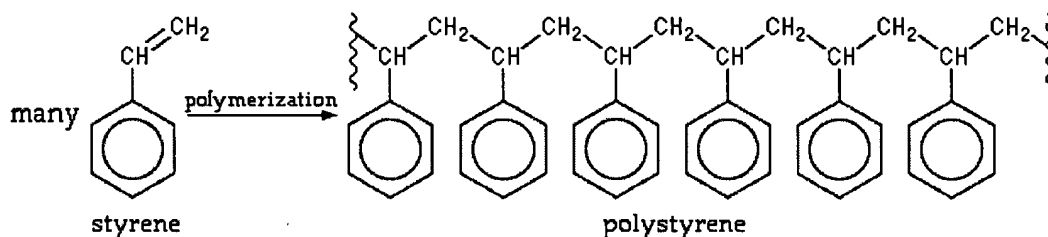
Solid foam

Polystyrene's most common use, however, is as expanded polystyrene (EPS). Expanded polystyrene is produced from a mixture of about 95% polystyrene and 5% gaseous blowing agent. The solid plastic is expanded into a foam through the use of heat, usually steam. Extruded polystyrene (XPS), which is different than expanded polystyrene, is commonly known by the trade name *Styrofoam*®. Expandable polystyrene is the lightweight material of which coffee cups and takeaway food containers are made. The voids filled with trapped air give expanded polystyrene low thermal conductivity. This makes it ideal as a construction material and it is used in structural insulated panel building systems. It is also used as insulation in building structures, as molded packing material for cushioning fragile equipment inside boxes, as packing "peanuts", as non-weight-bearing architectural structures (such as pillars), and also in crafts and model building, particularly architectural models. Foamed between two sheets of paper, it makes a more-uniform substitute for corrugated cardboard, tradenamed *Fome-Cor*.

Expanded polystyrene used to contain CFCs, but other, more environmentally-safe blowing agents are now used. Because it is an aromatic hydrocarbon, it burns with an orange-yellow flame, giving off soot, as opposed to non-aromatic hydrocarbon polymers such as polyethylene, which burn with a light yellow flame (often with a blue tinge) and no soot.

Production methods include sheet stamping (PS) and injection molding (both PS and HIPS).

The chemical makeup of polystyrene is a long chain hydrocarbon with every other carbon connected to a benzene ring.



A 3-D model would show that each of the chiral backbone carbons lies at the center of a tetrahedron, with its 4

bonds pointing toward the vertices. Say the -C-C- bonds are rotated so that the backbone chain lies entirely in the plane of the diagram. From this flat schematic, it isn't evident which of the phenyl (benzene) groups are angled toward us from the plane of the diagram, and which ones are angled away. The isomer where all of them are on the same side is called *isotactic* polystyrene, which isn't produced commercially. Ordinary *atactic* polystyrene has these large phenyl groups randomly distributed on both sides of the chain. This random positioning prevents the chains from ever aligning with sufficient regularity to achieve any crystallinity, so the plastic has no melting temperature, T_m . But metallocene-catalyzed polymerization can produce an ordered *syndiotactic* polystyrene with the phenyl groups on alternating sides. This form is highly crystalline with a T_m of 270°C.

Standard markings

The resin identification code symbol for polystyrene, developed by the Society of the Plastics Industry so that



items can be labeled for easy recycling, is **PS**. Unfortunately, the majority of polystyrene products are currently not recycled due to a lack of suitable recycling facilities. Furthermore, when it is "recycled," it is not a closed loop — polystyrene cups and other packaging materials are usually recycled into fillers in other plastics, or other items that can not be themselves recycled and are thrown away.

The Unicode character is ♸, which will appear here if you have a suitable font installed: .

Toughening

Pure polystyrene is brittle, but hard enough that a fairly high-performance product can be made by giving it some of the properties of a stretchier material, such as polybutadiene rubber. The two materials cannot normally be mixed due to the amplified effect of intermolecular forces on polymer solubility (see plastic recycling), but if polybutadiene is added during polymerization it can become chemically bonded to the polystyrene, forming a graft copolymer which helps to incorporate normal polybutadiene into the final mix, resulting in **high-impact polystyrene** or **HIPS**, often called "high-impact plastic" in advertisements. Common applications include use in toys and product casings. HIPS is usually injection molded in production.

Acrylonitrile butadiene styrene or ABS

(http://www.bpf.co.uk/bpfindustry/plastics_materials_Acrylonitrile_Butadiene_Styrene_ABS.cfm) plastic is similar to HIPS: a copolymer of acrylonitrile and styrene, toughened with polybutadiene. Most electronics cases are made of this form of polystyrene, as are many sewer pipes.

Styrene can be copolymerized with other monomers; for example, divinylbenzene for cross-linking the polystyrene chains.

Cutting and shaping

Expanded polystyrene is very easily cut with a hot-wire foam cutter, which is easily made by a heated and taut length wire, usually nichrome due to nichrome's resistance to oxidation at high temperatures and its suitable electrical conductivity. The hot wire foam cutter works by heating the wire to the point where it can vaporize foam immediately adjacent to it. The foam gets vaporized before actually touching the heated wire, which yields exceptionally smooth cuts. Polystyrene, shaped and cut with hot wire foam cutters, is used in architecture models, actual signage, amusement park and movie sets, airplane construction, and much more.

Polystyrene foam can easily be cut using a hot wire that melts the foam. Such cutters may cost just a few dollars (for a completely manual cutter) to tens of thousands of dollars for large CNC machines that can be used in high-volume industrial production.

Finishing

In the United States, environmental protection regulations prohibit the use of solvents on polystyrene (which would dissolve the polystyrene and de-foam most of foams anyway).

Some acceptable finishing materials are

- Water-based paint
- Mortar or acrylic/cement render, often used in the building industry as a weather-hard overcoat that hides the foam completely after finishing the objects.
- Cotton wool or other fabrics used in conjunction with a stapling implement.

See also

- Structural insulated panel
- ThermaSAVE

External links

- Tutorial on working with styrofoam (http://www.societyofrobots.com/materials_styrofoam.shtml)
- Macrogalleria: Polystyrene (<http://www.pslc.ws/mactest/styrene.htm>)
- Society of the Plastics Industry (<http://www.plasticsindustry.org/outreach/recycling/2124.htm>)
- DOW.com (<http://www.dow.com/styrofoam/>) – Styrofoam
- Bacteria Turns Styrofoam into Biodegradable Plastic (<http://www.sciam.com/article.cfm?chanID=sa003&articleID=0007B0AE-88AF-13FF-88AF83414B7F0000>)
- Polystyrene.org (<http://www.polystyrene.org/>)
- Arguments against polystyrene (<http://www.verdant.net/nofoam.htm>)

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